CROSSCUTTING TECHNOLOGY DEVELOPMENT AT THE CENTER FOR ADVANCED SEPARATION TECHNOLOGIES

SEMI-ANNUAL TECHNICAL PROGRESS REPORT

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DISCLAIMER

ABSTRACT

This Technical Progress Report describes progress made on the twenty nine sub-projects awarded in the second year of Cooperative Agreement DE-FC26-02NT41607: Crosscutting Technology Development at the Center for Advanced Separation Technologies. This work is summarized in the body of the main report: the individual sub-project Technical Progress Reports are attached as Appendices.

Note: SI is an abbreviation for “Le Systeme International d’Unites.”

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INTRODUCTION

The U.S. is the largest producer of mining products in the world. In 2003, U.S. mining operations produced $57 billion worth of raw materials that contributed a total of $564 billion to the nation's wealth. Despite these contributions, the mining industry has not been well supported with research and development funds as compared to mining industries in other countries. To overcome this problem, the Center for Advanced Separation Technologies (CAST) was established to develop technologies that can be used by the U.S. mining industry to create new products, reduce production costs, and meet environmental regulations. Originally set up by Virginia Tech and West Virginia University, this endeavor has been expanded into a seven-university consortium – Virginia Tech, West Virginia University, University of Kentucky, University of Utah, Montana Tech, New Mexico Tech and University of Nevada, Reno - that is supported through U.S. DOE Cooperative Agreement No. DE-FC26-02NT41607: Crosscutting Technology Development at the Center for Advanced Separation Technologies.

Much of the research to be conducted with Cooperative Agreement funds will be longer-term, high-risk, basic research and will be carried out in five broad areas:

a) Solid-solid separation
b) Solid-liquid separation
c) Chemical/Biological Extraction
d) Modeling and Control, and
e) Environmental Control.

Distribution of funds is handled via competitive solicitation of research proposals through Site Coordinators at the seven member universities. These were first reviewed and ranked by a group of technical reviewers (selected primarily from industry). Based on these reviews, and an assessment of overall program requirements, the CAST Technical Committee made an initial selection/ranking of proposals and forwarded these to the DOE/NETL Project Officer for final review and approval. The successful projects are listed below by category, along with brief abstracts of their aims and objectives.

a) Solid-Solid Separation

1. Development of Novel Ultrafine Sizing Methods (Joint UK/VT Project) (KY001/VA008)

Principal Investigators: R.-H. Yoon and G.H. Luttrell, Virginia Tech
Principal Investigators: R.Q. Honaker and BK. Parekh, University of Kentucky
Period of Performance: May 1, 2003- October 31, 2006 (2-Year Project)

The conventional techniques employed for sizing ultrafine particles in the coal and mineral processing industries have inherent inefficiencies that negatively impact on separation performance and production costs. In light of this problem, a broad based R&D program is proposed to investigate several innovative techniques for fine particle sizing. The processes to be evaluated will include a wide array of mechanical, hydraulic, and novel approaches for fine

particle sizing. For each process, detailed tests programs will be conducted to optimize operating parameters so that maximum efficiency and capacity can be achieved while maintaining particle size cuts in the 25-50 μm size range. The resultant test data will be used to mathematically simulate different circuit arrangements for the most promising technologies. A detailed economic study will be performed for those circuits that have the greatest potential for commercialization and industrial implementation. Due to the large scope of this project, the proposed work will be conducted as a joint effort between researchers at the University of Kentucky and Virginia Tech.

2. Dispersion and Flotation of Clays from New Mexico Potash Ores (NM001)
Principal Investigators: I. Gundiler, S. Titkov, and M. Yekeler, New Mexico Tech
Period of Performance: May 1, 2003-October 31, 2006 (1-Year Project)

New Mexico is the largest potash producer in the United States, supplying 70% of the domestic consumption of agricultural fertilizers. Potash mining began in the Carlsbad potash district in the early 1940s and while there are still vast reserves of potash minerals, producers are now dealing with low grade ores contaminated with clays and water-soluble magnesium minerals, which adversely affect the flotation of sylvite (KCl). Sylvite is floated from saturated brines with cationic collectors. The clays present in these brines absorb flotation reagents (thus increasing reagent costs), decrease recoveries of sylvite, contaminate the product and increase energy consumption for dewatering and drying. These clays are dispersed during grinding and/or attrition scrubbing and are then removed by hydrocyclones ahead of flotation. However, significant amounts of clay are carried over into flotation, where they are further dispersed by the mechanical action of impellers, thus hindering flotation. Furthermore, elevated brine temperatures during the summer affect collector adsorption on clays, depressing sylvite flotation. The presence of high concentrations of magnesium ions in the brine, which is peculiar to this district, also affects recoveries.

These technological problems must be solved for the state potash industry to remain viable and competitive. This study will investigate means of improving clay dispersion using organic and inorganic dispersants to increase the efficiency of slimes removal in existing facilities, and will study the effects of elevated magnesium ion concentrations and elevated temperatures on the flotation of sylvite. Clay flotation, which has been shown to be superior to hydroseparators for clay removal in foreign operations, will also be investigated.

3. Flotation Technology for the Trona Industry (UT001)
Principal Investigator: Jan D. Miller, University of Utah
Period of Performance: May 1, 2003- October 31, 2006 (2-Year Project)

Soda ash (Na_2CO_3) produced from the trona deposits of the Green River Basin in Wyoming by chemical treatment is valued at approximately $800 million per annum. Existing process technologies for the production of soda ash from trona involve dissolution in hot brine, drying, sedimentation and filtration for the removal of impurities, and subsequent crystallization and calcination for the recovery of soda ash. In this regard, mining and operating costs, particularly energy costs, are higher than desired. A preferred

processing strategy might be to remove gangue mineral contaminants from the plant feed prior to dissolution in hot brine. It is expected that in this way improved productivity can be achieved in addition to significant savings in energy. Such a preprocessing strategy at ambient temperature and pressure has been limited by the lack of satisfactory process technology. Now based on recent results from laboratory research at the University of Utah it seems that the run-of-mine trona ore can be treated at ambient temperature and pressure using a special flotation procedure to separate the gangue minerals and make a trona concentrate with a purity of almost 99% trona at a recovery of more than 97%. Development and utilization of this new technology will allow for energy conservation, improved resource utilization, increased productivity and the development of a new product for the marketplace. In this regard a two-year research program involving industrial participation is proposed to develop the technology and demonstrate its effectiveness at a plant site.

4. Flotation Processes/Experiments and Analysis (VA009)

Principal Investigators: D. Telionis and P. Vlachos, Virginia Tech
Period of Performance: May 1, 2003- October 31, 2006 (2-Year Project)

Flotation processes involve complex, three-phase flow interactions between a liquid, air bubbles and solid particles. For decades, engineers and researchers based their calculations on algebraic formulas that model these interactions. These formulas were derived from simple models, experimental data and/or arbitrary assumptions. Considerable progress has been made but this approach is still far from providing a reliable tool for the design of flotation machines.

We will take a more rigorous approach to the analysis and modeling of the flotation process. The proposed effort will combine detailed theoretical analysis and modeling with state-of-the-art, global, multi-phase flow measurements to quantify the effects of the various hydrodynamic parameters on the flotation process. We will employ a Digital Particle Image Velocimeter (DPIV) that can record velocity vectors of all three phases. We will measure three-phase flow interactions of bubbles and model particles of different hydrophobicity with a turbulent flow field. We will deliver global, time-resolved velocity distributions and turbulence characteristics for each phase. Our modeling approach will incorporate all physical parameters that affect the collision efficiency of coal particles and flotation bubbles and the probabilities of attachment and detachment. An advanced model for predicting and quantifying the efficiency of the flotation process will be the final deliverable of this two-year effort. Such a tool will improve the design of flotation equipment and/or enhance the performance of existing systems.

5. Column Flotation of Relative Coarse and Fine Dolomitic Phosphate Pebbles (WV009)

Principal Investigator: Felicia F. Peng, West Virginia University
Period of Performance: May 1, 2003- October 31, 2006 (2-Year Project)

Dolomite in phosphate flotation concentrates is troublesome for down-stream operations. High dolomite contents cause higher consumption of sulfuric acid, reduce filtration rates and lower $P_2 0_5$ content in the fertilizer manufacturing process. However,

the separation of dolomite particles from phosphate minerals is difficult because the dolomite is finely disseminated throughout the phosphatic pebbles and both are oxide type minerals with the same cationic component. Thus, they show similar electrokinetic, adsorptive and desorptive behavior in physical separation process such as flotation. Various flotation processes have been developed in the past four decades, but none is satisfactory due to high MgO content and/or low overall P_20_5 recovery in the final phosphate concentrate. In this research project, dolomitic phosphate pebbles from Florida will be treated by column flotation. A liberation analysis of the dolomite-phosphate matrix will be conducted to determine optimum grinding conditions; new selective mixtures of fatty acid collectors and non-ionic surfactants will be evaluated on relatively coarse (minus 300 microns) and fine (minus 150 microns) dolomite particles; appropriate mixtures of phosphoric acid/sulfuric acid will be used to depress phosphate particles; and the effect of addition of non-ionic surfactants on the separation performance will be determined. The goal is to produce a phosphate concentrate containing 30% P_20_5 and less than 1.0% MgO contents at high P_20_5 recoveries from low grade phosphatic pebbles stockpiled at plant sites and from pebbles generated from mining lower grade reserves.

6. Beneficiation of Mixed Potash Ores From New Mexico (NM004)

Principal Investigator: Ibrahim Gundiler, Lynn Brandvold, Tanja Pietraß, Stanislav Titkov, New Mexico Tech

Period of Performance: May 1, 2004- October 31, 2006 (2-Year Project)

New Mexico is the largest potash producer in the United States, which supplies 70% of the domestic production for agricultural fertilizers. Potash mining began in the Carlsbad potash district, in the southeastern corner of the state, in early 1940s. Although, there are still vast reserves of potash minerals, clean, high-grade ores are depleted. Sylvite (KCL) and langbeinite are the major minerals mined in the district, and New Mexico is the only location in the world where langbeinite concentrates are produced. Langbeinite, a double salt of potassium and magnesium, is the preferred form of potassium fertilizers for plants, which can not tolerate chloride ions.

Sylvite flotation in carried out from saturated brines with cationic collectors. Clay minerals adsorb flotation reagents, thus increase reagent costs and reduce recovery of sylvite. Therefore, clays are dispersed during grinding and in attrition scrubbers, and removed by hydrocyclones. Furthermore, elevated brine temperatures during the summer also affect collector adsorption on clays, depressing sylvite flotation. Presence of high concentrations of magnesium ions, which is peculiar to this district, also affects the recovery.

Langbeinite ores are concentrated by gravity separation in coarse sizes and further cleaned by leaching halite (NaCl) with water. Some impurity minerals, which have similar specific gravity and solubility in water, however, contaminate the product. The present concentration process is water-intensive and availability of fresh water in drought-stricken southwest is becoming increasingly sensitive issue. Furthermore, as the high grade ores are depleted, mixed sylvite-langbeinite ores and langbeinite- kieserite ores have to mined and processed. Technology for efficient separation of these minerals is not available, and, usually, one or more of the potash minerals are lost to the tailings.

For the potash industry of the state to remain viable and competitive, these technological problems have to be solved. This study will address to improve sylvite flotation from mixed ores in brines containing high concentrations of magnesium ions, and develop new flotation method for separation of sylvite, halite, and kieserite from mixed langbeinite ores.

Finally, the effect of elevated magnesium ion concentrations and elevated temperatures on the flotation of sylvite will be investigated. Flotation studies will be augmented with fundamental studies to investigate the hydration of KCl surfaces in Mg-containing brines using the Nuclear Magnetic Resonance, proton relaxation techniques, and changes in morphology and surface composition will be investigated using Atomic Force Microscopy and Electron Microprobe techniques. This study is expected to produce tangible results to improve the efficiency of the existing plants and contribute to the understanding of sylvite flotation from magnesium bearing brines, and soluble salt flotation in general.

7. Development of New Reagents for the Flotation of Dolomite from Phosphate Ore (NV002)

Principal Investigators: Maurice C. Fuerstenau, Manoranjan Misra and Thomas W. Bell, University of Nevada, Reno
Period of Performance: May 1, 2004- October 31, 2006 (2-Year Project)

The United States is the largest producer of phosphate rock in the world, which corresponds to 30% of the world production. Florida accounts for 80% of the U.S. phosphate production. During the past century, the Florida phosphate industry has produced high quality phosphate with low MgO (< 0.5%) content. As low dolomitic phosphate reserves become exhausted, the remaining deposits contain lower amounts of phosphate with significantly higher dolomite (MgO) content. It is generally difficult to obtain a phosphate concentrate from such materials containing less than the desired MgO content of 1% MgO. The objective of the research work is to evaluate the effectiveness of new synthesized collectors for the selective flotation of dolomite from phosphate rock. The experimentation will include evaluating the applicability of the new collectors through adsorption, electrokinetic and microflotation studies, and the flotation of dolomitic phosphate ores from Florida, Utah and Idaho

8. High Frequency Eddy Current Separation of Metallicic Residue from Slags, Sands, Electronic Scrap and Other Wastes (UT004)

Principal Investigators: Raj K. Rajamani, University of Utah
Period of Performance: May 1, 2004- October 31, 2006 (2-Year Project)

The proposed work is to separate metallic grains from sands, slags or electronic scrap by means of a novel device called High Frequency Eddy Current Separator. The dry mixture of foundry sands is passed through the gap between the poles of a magnet. The metallic granules are repelled from the falling stream of sand, and hence are separated. This device has many technical and commercial advantages over the existing technologies (i.e.

lower cost, no use of water or chemicals, absence of polluting gases, etc.).
A high frequency magnetic field is generated in the gap when radio-frequency current is passed through windings on a ferrite core. As the electrically conducting particle enters the field, an electromotive force (emf) is generated on the particle itself. Due to the emf, an eddy current flows on the particle. These currents, in turn, induce their own magnetic field around the particle. Lenz rule of physics states that the induced magnetic field is directly opposed to the original or imposed oscillating field. Hence, the particle experiences a repelling force. The repelling force depends on the strength of the magnetic field, the frequency of oscillations, and the cross-sectional area and electrical conductivity of the particle.

The object of this program is to develop third prototype for testing. The prototype engineering is based on the first lab unit developed at the University of Utah and the second lab unit built by EMPS Corporation, Salt Lake City, Utah. These two units used a ferrite toroid and a bi-polar amplifier to generate the high frequency magnetic field in the gap of the toroid. Invariably the choice of ferrite core limited the gap dimensions to about 10X10 mm. The unit proposed here is a larger toroid with 125 X125 mm gap to be driven by a direct drive electronic circuitry. This unit would be capable of processing 100 lb./hr of solid stream and hence suitable for process optimization and operating parameter study.

Present eddy-current devices, have been confined to the recovery of large aluminum cans from municipal wastes. For example Eriez Magnetics has a line of eddy current separators, which uses permanent magnets of alternating polarity spinning at high speeds under a belt conveyor. Hence this unit can only produce about 1 kHz frequency. Low frequency devices can separate only larger pieces, of size ½ inch, of metal. The proposed high-frequency separator uses magnetic-field frequencies of 50 to 100 kHz that enhances its ability to separate much smaller grains of size larger than 0.2 mm.
In copper production, both a copper-sulfur matte and a blister copper are formed, which are covered by a slag layer. In the production of aluminum and magnesium, electrolytic cells are used to electrowin the liquid metal at the cathode. A slag layer is also present in this process. Typically, there is mixing at the liquid metal/slag interface, which results in droplets or prills of metal suspended in the slag phase. Approximately 3.6 million metric tons each of copper and phosphorous slag are produced each year in the U.S. The annual production of nickel, lead and zinc slag is estimated at 0.45 to 0.9 million metric tons. Electric and electronic goods comprise a vast and diverse spectrum of items that are sent to the landfills each year. A 1991 study estimates that 150 million personal computers and workstations will have been sent to landfills by the year 2005. The recovery of metallic copper, gold, palladium and aluminum from scrap is in the best interest of environmental protection. These waste streams are typical application targets for the high frequency separator proposed here.

9. Continuation of Project WV002 - Dry Particle Separation in a CFB Riser System (WV009)

Principal Investigator: Eric Johnson and Bruce W. Kang, West Virginia University
Period of Performance: May 1, 2004- October 31, 2006 (2-Year Project)

The proposed project is a continuation of the study to determine the potential for separating small dense particles from small light particles in a CFB riser system. This exploratory work led to many interesting and practical results. It is proposed to now refine and expand our test conditions and develop a more comprehensive analysis of the results. The experimental conditions planned for this continuation project are 1) more closely matched particle size distributions for the heavy and light particles in the mixture, 2) smaller density difference between the heavy and light particles, 3) separation of particles based only on size differences, and 4) developing and employing a larger diameter riser to study the scaling of the separation processes in a riser.

10. Studies of Froth Stability and Model Development (VA002)
(Continuation from CAST I)
Principal Investigator: Roe-Hoan Yoon, Virginia Tech
Period of Performance: May 1, 2004- October 31, 2006 (2-Year Project)

Froth plays an important role in flotation. It determines the final grade of the product and the maximum carrying capacity (or throughput) of a flotation machine. Also, many operators use stronger frothers to produce smaller air bubbles and, hence, higher recovery and throughput. Despite its importance, little is known of the fundamentals of foam and froth stability. It is, therefore, proposed to study the various factors affecting the stability of flotation froth. This will be accomplished by using the thin film balance (TFB) technique of Scheludko and Exerowa (1959) and by monitoring the stability of froth in a bubble column using a video camera. The results will be used for developing a froth model and also for developing effective defoamers.

11. Direct Measurement of Forces in Flotation (VA004)
(Continuation from CAST I)
Principal Investigator: Roe-Hoan Yoon, Virginia Tech
Period of Performance: May 1, 2004- October 31, 2006 (2-Year Project)

The objective of this project is to directly measure the interaction force between a particle and bubbles as a function of separation distance. This force controls the attachment and detachment of particles to bubbles, which is an essential step in determining the efficiency of a flotation process. A specially designed device will be fabricated for these measurements. The device will use the force-detection method employed by an Atomic Force Microscope and the separation-detection method employed by a Surface Forces Apparatus. The key advances are to explicitly measure both the separation between the particle and the bubble and the shape of the bubble at all times. Without this separation and shape data, it would be difficult to relate the measured forces to flotation results. After fabrication of the device, measurements of the interaction forces acting on hydrophilic, hydrophobic, and charged particles in aqueous solutions of surfactant molecules will be obtained.

12. Enhanced Flotation Performance Through Column Froth Enrichment (KY006)
Principal Investigators: Rick Q. Honaker and Daniel Tao, University of Kentucky
Period of Performance: June 1, 2005-May 31, 2005 (2-Year Project)

Froth flotation is a process that separates particles based on their differences in physical and surface chemistry properties. For fine feed material that is comprised of particles having wide degrees of floatability, selectivity is often optimized by maximizing the differences in the flotation rates between the particles targeted for recovery in the froth concentrate and those needed to report to the underflow stream. The benefits of differential flotation rates are realized in the collection zone of a flotation system where bubble-particle collision and attachment occurs. However, selectivity between particles of varying floatability can be significantly enhanced in the froth zone through a reflux mechanism that circulates detached particles back to the collection zone. Particle detachment in the froth zone occurs due to bubble coalescence, which leads to an insufficient amount of bubble surface area to carry all of the material recovered in the collection zone. Based on previous research, the detachment process is selective in that particles having a lower degree of floatability (or hydrophobicity) are preferentially released from the bubble surfaces. Selectivity through the detachment process can be improved by the addition of a more hydrophobic material into the froth zone and possibly by recycling a portion of the flotation concentrate, thereby enriching the flotation froth.

In a recent study, froth zone and overall flotation recovery values were quantified for particles in an anthracite coal that were characterized as having wide differences in floatability potential. The unique aspect of the coal was the presence of 'bone' material in the high density fractions which had a relatively high degree of floatability. As a result, the minimum product grade achieved by froth flotation was about 15% despite washability data indicating the potential for achieving a product containing nearly 3% ash. Highly floatable material was added directly into the froth zone while treating the anthracite coal and then removed from the product and tailing samples using density fractionation. The enriched froth phase reduced the product ash content of the anthracite product by 5 absolute percentage points while maintaining coal recovery at the same level. These results support the findings of previous fundamental research conducted on hematite flotation with the addition of hydrophobic silica directly into the froth phase.

The proposed two-year project will further investigate the fundamentals of the detachment process as well as develop unique methods of commercial application that may be more useful for sulfide and precious mineral industries. Plastic material that contains an amount of magnetite that makes the plastic easily recoverable by a low-intensity magnetic separator will be directly added in the flotation froth through the wash water distributor of a flotation column. By varying the formulations of the plastic, surface hydrophobicity and thus floatability can be controlled. Initial tests will involve the flotation of silica that will be methylated to achieve varying degrees of floatability. External refluxing of a portion of the flotation froth will also be investigated using the methylated silica. To evaluate the commercial benefits, the improved selectivity achieved by froth enrichment using external refluxing and the addition of the magnetic material will be accessed for the flotation of coal, sulfide minerals and phosphate.

13. Engineering Development of a Fine Particle Heavy Medium Separator (VA012)
Principal Investigators: Gerald H. Luttrell, Virginia Tech and Robert Moorhead, Krebs Engineers, Inc
Period of Performance: June 1, 2005-October 31, 2006 (2-Year Project)

The objective of this project is to develop an innovative heavy medium separator that can reduce the cost and improve the efficiency of fine coal cleaning. The technology is designed to replace inefficient water-based separators such as spirals and water-only cyclones that are currently used by industry to upgrade 1 x 0.15 mm run-of-mine coal. The new heavy medium separator incorporates novel design features that allow it make sharp separations without the need for costly micronized magnetite. As a result, the new technology can share circulating medium from other circuits, thereby avoiding the expense of installing and maintaining an additional medium circuit. These advantages, together with the low headroom design of the module, make it possible to integrate this technology into an existing plant with minimal retrofit costs. The project tasks will include (i) design and construction, (ii) pilot-scale testing, (iii) field testing, and (iv) flowsheet development

14. Improved Destruction and Control of Residual Flotation Froths (VA014)
Principal Investigators: Gerald H. Luttrell and Roe-Hoan Yoon, Virginia Tech
Period of Performance: June 1, 2005-October 31, 2006 (2-Year Project)

Flotation froths containing large amounts of ultrafine particles can become excessively stable and create serious handling problems for coal preparation plants. Steps taken by operators to combat these problems, such as lowering the frother dosage, have resulted in large reductions in fine coal recovery and plant profitability. The objective of this project is to develop and evaluate several improved methods for the control and destruction of residual flotation froths. The first phase of the proposed work will focus on a detailed laboratory study of the physical and chemical parameters that impact froth stability. These studies will be followed by in-plant sampling campaigns at several coal plants to establish how frothing agents partition within different circuits and to determine whether modifications to the layout or dilution practices can minimize handling problems. The data obtained from these investigations will be used to develop improved mechanical and chemical methods for froth control/destruction at an industrial plant site

15. Development of a Turbulent Flotation Model and a Computer Simulator (VA015)
Principal Investigators: Roe-Hoan Yoon and Gerald H. Luttrell, Virginia Tech
Period of Performance: June 1, 2005-October 31, 2006 (2-Year Project)

Flotation is the most widely used method of separating fine particles in the mining industry. The method of using air bubbles was awarded a U.S. patent in 1905, exactly 100 years ago. Yet, there are no flotation models incorporating both surface chemistry (e.g., hydrophobicity, ζ-potential, and surface tension) and hydrodynamic (e.g., bubble size, particle size, energy dissipation) parameters under turbulent flow conditions. It is, therefore, proposed to develop a comprehensive flotation model incorporating practically all of the process variables employed in flotation practice. The turbulent flotation model

will be able to describe the events taking place in both the pulp and froth phases. Laboratory experiments will be carried out to verify the model, and model will be transformed into a compute simulator that can predict complicated flotation circuits incorporating rougher, scavenger and cleaner operations.

16. **Novel Surfactants as Collectors for Froth Flotation (VA015)**
Principal Investigators: Richard D. Gandour, Virginia Tech
Period of Performance: June 1, 2005-October 31, 2006 (2-Year Project)

Our goals are to synthesize and study novel, inexpensive amphiphiles that can perform as co-surfactant collectors in mineral flotation. These surfactants will selectively bind to particles and create a hydrophobic coating on a particle. These novel surfactants will bind more selectively and provide hydrophobic sites where cheaper, less-selective collectors can bind. These novel surfactants have very hydrophobic, long chains, yet are sufficiently water soluble for mineral processing and coal-fines processing. These amphiphiles, which we call 'hydra surfactants', will have two tails and three heads. These novel molecules will be useful for many different separations in mineral processing.

17. **Measurement of Surface Forces Between Hydrophobic Surfaces**
Principal Investigators: Roe-Hoan Yoon, Virginia Tech
Period of Performance: June 1, 2005-October 31, 2007 (2-Year Project)

Froth flotation is the most widely used method of separating fine particles in the mining industry. The process is based on rendering a selected mineral hydrophobic, so that it can be separated from other minerals that are hydrophilic. Thus, control of particle hydrophobicity is critically important in flotation. However, the nature of the hydrophobicy is not fully understood, particularly in view of the forces acting between two hydrophobic particles suspended in water. In the proposed work, surface force measurements will be conducted using an atomic force microscope (AFM). The force measurements will be conducted with gold, sulfide minerals, and rutile after coating them with thiols, xanthates, and anionic and cationic surfactants. In addition, the surfaces will be characterized in terms of their acid-base properties, infrared spectra, and AFM images. The results will be useful for better understanding the nature of hydrophobicity and, hence, furthering the flotation technology.

b) Solid-Liquid Separation

1. **Improving Densification of Fine Coal Refuse Slurries to Eliminate Slurry Ponds (KY002)**
Principal Investigators: B.K. Parekh and R.Q. Honaker, University of Kentucky
Period of Performance: May 1, 2003-May 31, 2005 (2-Year Project)

Increased mechanization in underground coal mining has increased the volume of refuse generated by coal preparation plants. The fine refuse slurry, composed of coal and mineral matter, is usually disposed of in a holding pond (impoundment), but incidents of impoundment breakthrough have forced the industry to look for alternative methods for fine refuse storage in the future. The main objective of the proposed program is to

evaluate a new technique known as "Paste Thickening Technology," which utilizes a DORR-OLIVER EIMCO DEEP CONE Thickener to discharge the waste slurry as a paste. The paste material should be stackable at low repose angles and would dry over a period of time, thus avoiding the storage of slurries in ponds. The proposed study will be conducted on coal waste slurries obtained from two different preparation plants. Laboratory studies will involve the characterization of the slurries, bench-scale flocculation studies and rheological analysis of the flocculated materials to identify yield stresses at various solid concentrations. This information will be used to establish optimum conditions for the production of a thickened paste product. A pilot-scale study will then be conducted at one of the coal preparation sites to obtain technical and economic data for a commercial installation and operation. It is anticipated that the outcome of the study will be an effective and economical process for the safe disposal of fine coal refuse.

2. Development and Testing of a Horizontal Pressure Belt Filter (VA010)
Principal Investigators: R.-H. Yoon & G.H. Luttrell, Virginia Tech
Period of Performance: May 1, 2003- October 31, 2006 (2-Year Project)

A variety of mechanical processes are available for dewatering fine particles in the coal and mineral processing industries. Unfortunately, many of these processes suffer from major shortcomings such as poor dewatering performance, low throughput capacity, and high capital and operating costs. This project seeks to overcome these problems by developing a new type of dewatering process that combines the operational flexibility of a continuous belt filter with the dewatering efficiency of a batch pressure filter. The proposed project involves the design, construction, testing, and evaluation of a prototype unit and pilot-scale test circuit having a production capacity of approximately 100 lb/hr. Test data obtained from the project will be used to promote the engineering development of a full-scale commercial unit.

3. Development of a Fine Particle Centrifuge (VA006)
(Continuation from CAST I)
Principal Investigators: G.H. Luttrell & R.-H. Yoon, Virginia Tech
Period of Performance: May 1, 2004- October 31, 2006 (2-Year Project)

The solid-solid separation processes employed by modern coal preparation plants require large amounts of process water. After cleaning, the unwanted water must be removed from the surfaces of the particles using mechanical dewatering equipment. Coarse particles can be readily dewatered using simple screening systems, while finer particles require more complicated unit operations such as centrifuges and filters. Unfortunately, the processes used to dewater fine particles are inherently inefficient and expensive to operate and maintain. To overcome these problems, a novel centrifugal filter has been developed by researchers at Virginia Tech. Preliminary test data suggest that this new technology can reduce the moisture content of fine coal products by approximately 30-50% compared to existing dewatering processes. The objective of this project will be to construct a continuous prototype unit and to conduct a detailed experimental

investigation of this new technology.

4. Improvements in Screen Bowl Centrifuge Performance (VA013)
Principal Investigators: Robert C. Bratton & G.H. Luttrell, Virginia Tech
Period of Performance: May 1, 2004- October 31, 2006 (2-Year Project)

Screen-bowl centrifuges are the most commonly used method for dewatering fine coal in the United States. Unfortunately, this process is the least efficient and most costly dewatering operation in the preparation plant. The work outlined in this proposal will seek to develop an improved understanding of the operating characteristics and technical capabilities of screen-bowl centrifuges. Plant operators will be able to use this fundamental knowledge to improve the performance of their dewatering circuits and improve plant profitability. In addition, several new screen-bowl centrifuge features will be developed and evaluated as part of the proposed work. The innovations will include the development and testing of internal injection ports for (i) adding flocculant to the low-solids pool and (ii) adding dewatering aids and surface tension modifiers to the dewater screen solids. These technological enhancements are expected to improve moisture reduction and increase fine coal recovery

c) Chemical/Biological Extraction

1. Bio-Assisted Heap Leaching of Nickel Laterites for the Development of a Domestic Nickel Industry (UT002)
Principal Investigator: S. Duyvesteyn, University of Utah
Period of Performance: May 1, 2003- October 31, 2006 (2-Year Project)

The U.S. currently imports all of its nickel, which is a strategic material used in stainless steels and other corrosion-resistant materials. Existing U.S. resources are worth around $10 billion at current metal prices, but occur mostly in low-grade laterite deposits, for which conventional hydrometallurgical processes are not economically feasible production routes. These processes typically utilize mineral acids that cannot be recycled economically and can cause significant environmental problems. The solubilization of metal ions from ores by organic acids produced by microorganisms has been demonstrated to be a viable alternative for metal production with reduced environmental and remediation issues, as organic acids are readily biodegradable. The fact that many of these organic acids and other metabolites form strong chelating complexes with the base metal ions also results in a reduction in the acid requirements to achieve complete solubilization.

This research proposal involves a biotechnological approach, called bio-assisted heap leaching (BAHL), for the production of nickel metal from low-grade ore synergistically with the co-production of citric acid. The BAHL process can be described as follows: laterite nickel ore is combined with an organic nutrient and put on heaps where fungi, such as Aspergillus niger, produce organic acids during their natural metabolic cycle. Recycle solution is sprayed over the heaps and its percolation through the heaps results in

the dissolution of nickel. The resulting nickel-containing leach solution is collected and the nickel and citrate values are recovered.

2. **The Development and Utilization of Alkaline Sulfide Leaching and Recovery of Gold (MT001)**
   Principal Investigator: C. Anderson and L.G. Twidwell, Montana Tech
   Period of Performance: May 1, 2003- October 31, 2006 (2-Year Project)

   Due to the increasing concerns over the emission of sulfur dioxide from roasting and smelting, there has been an increased interest in pressure oxidation as a means of treating gold bearing ores and concentrates. One of the problems with the partial oxidation of the sulfide host matrix to form elemental sulfur is that sulfur containing streams are difficult to treat using cyanidation. In the present study, the alkaline sulfide system will be studied as an alternative to cyanide for recovering gold from elemental sulfur. A complete thermodynamic model of the alkaline sulfide gold leaching system will be developed using Stab-Cal software and the leaching system and its kinetics will be optimized.

3. **Hydrometallurgical Processing of Chalcopyrite Concentrates (NV001)**
   Principal Investigator: M. Misra and M. Fuerstenau, University of Nevada, Reno
   Period of Performance: May 1, 2003- October 31, 2006 (2-Year Project)

   Hydrometallurgical processing of chalcopyrite at moderate temperature and pressure has been a goal of the copper industry for decades. Research has shown that a protective sulfur layer forms on chalcopyrite when leached with ferric salts in acidic medium. This layer limits the transport of electrons from the mineral surface to the oxidant and precludes the use of this technology for chalcopyrite processing. Research at the University of Nevada, Reno has shown that the introduction of finely-divided silica improves the kinetics of leaching dramatically. Silica adsorbs on the surface of chalcopyrite, and since it is an n-type conductor, conduction of electrons from the mineral surface to the oxidant occurs by photocatalysis of the sulfur product layer. Dissolution amounts of as much as 80% have been achieved under the limited conditions examined, namely at atmospheric pressure and 50°C.

4. **Simultaneous Electrolysis of Copper and Ferrous Ions to Produce Copper Cathode and to Regenerate Ferric Sulfate - The Lixiviant to Dissolve Copper Sulfide Minerals (MT002)**
   Principal Investigator: C. Young, H.-H. Huang and C. Fabian, Montana Tech
   Period of Performance: May 1, 2003- October 31, 2006 (2-Year Project)

   Copper leaching is primarily conducted on oxidized ore bodies at low pH by using sulfuric acid (H_2SO_4). The sulfate acts as the lixivant to solubilize the copper as copper sulfate ($CuSO_4$). An oxidant is also needed to enhance reaction rates – typically this is dissolved oxygen ($O_{2)}$ and/or ferric (Fe^{3+}) ion. The dissolved copper must then be extracted from the water to separate it from other dissolved constituents including iron. Traditional solvent extraction and electrowinning (SX/EW) procedures do this and ultimately yield quality copper cathode as product. After SX/EW, leach solution is

recycled to the leaching process and replenished with oxidant as needed. For example, biological activity can regenerate ferric ions or mechanical agitation can produce dissolved oxygen (which in turn can regenerate ferric ions).

Ferric ions can also be regenerated electrolytically and simultaneously to copper cathode production. This is the basis of the proposed research. To accomplish this, a porous membrane will be used to keep the anode and cathode compartments separated and modern rotating cylinder electrodes will be used to stir solutions, obtain high current densities and ultimately produce superior grade copper cathode. Although it is possible to avoid the SX step, it will be used to produce two streams: raffinate, which will go to the anode compartment where ferric is regenerated, and pregnant or advance solution, which will be go to the cathode compartment where copper metal is produced. Various chemicals and additives may have to be added to control copper cathode formation and thereby avoid, for example, dendritic growth. Preliminary cost analyses show that copper can be produced for approximately $0.30/lb with this new, more energy efficient, technique.

5. Ion Exchange Recovery of Cobalt from Copper Leach Solutions (NM002)
Principal Investigator: I. Gundiler and M. Hatch, New Mexico Tech
Period of Performance: May 1, 2003- October 31, 2006 (2-Year Project)

Cobalt is a strategic and critical metal which is used in production of super alloys for use in jet engine turbines, wear and corrosion resistant alloys, cutting tools, magnets and various other alloys and chemicals. It is not mined or refined in the United States; therefore, 80% of the cobalt consumed in the U.S. is imported. The remaining balance is met with recycled alloys and supplies from stockpiles. Although there is historical production and known reserves, these are not economical to exploit at the present. However, there is a readily available source of cobalt in the leach solutions generated in large copper mining operations in the Southwestern U.S. If only a fraction of this cobalt could be recovered, New Mexico and Eastern Arizona copper leach operations could potentially supply 20% of U.S. imports. Currently, the technology to recover the metal from these solutions economically is not available.

Ion exchange processes could recover this cobalt. However, commercially available resins are either too expensive, or do not function in acidic solutions. Absorption kinetics of these resins are also fairly slow. Three new resins will be synthesized at New Mexico Tech for copper and cobalt recovery from acidic solutions. The resins will be characterized and tested in the laboratory using pure chemicals, as well as process solutions to be obtained from the Phelps Dodge Mining Company, New Mexico operations. The performance of the synthesized resins will also be compared with that of commercially available resins.

6. The Effect of Diphenyl Oxide Surfactants on Nucleation and Growth of Potassium Sulfate Crystals: Development of Enhanced Surfactants for the Potash Industry (NM003)
Principal Investigator: G. Bond and C. Hockensmith, New Mexico Tech

Period of Performance: May 1, 2003- October 31, 2006 (2-Year Project)

Surfactant-controlled crystallization leads to an increase in the efficiency of potassium sulfate production, particularly when alkyl diphenyl oxide-type (ADO) surfactants are employed in synthesis. Improved control of crystallization in both the initiation and termination phases can increase the ratio of granular particles to fines, decreasing costs associated with production and facilitating the utilization of lower-grade ores. Mother liquors in potash extraction contain high percentages of magnesium as well as other ions including chloride and impurities such as clay and silica. Potassium sulfate crystals will be produced in the presence of different ADO surfactants, and evaluated by SEM, TEM, XRD, FTIR and AFM. Crystallization processes, particularly those that affect crystal morphology, size, initiation and termination, will be studied in relation to the surfactant effect. This information will be used to improve control of potassium sulfate precipitation and develop the next generation of surfactants to facilitate extraction of granular potassium sulfate.

7. **Overcoming Technological Barriers to More Efficient Recovery of Copper from Chalcopyrite (UT005)**
   Principal Investigator: Michael L. Free, University of Utah
   Period of Performance: May 1, 2004- October 31, 2006 (2-Year Project)

   Extraction and recovery of copper from chalcopyrite is one of the most important processes in the nonferrous metals industry. It is currently performed using smelting, converting, and electrorefining, yet it also necessitates by-product sulfuric acid production at a rate of three tons of acid per ton of copper. Efforts to convert this process to leaching, solvent extraction, and electrowinning, which is a lower cost alternative to the smelting, converting, and electrorefining process that is practiced for most other copper minerals, have been unsuccessful. However, new technologies, such as halide leaching and electrowinning offer significant economic and environmental advantages over the current industrial practices.

   Halide leaching and electrowinning requires only 25% of the energy needed to electrowin copper using traditional sulfate-based solution technology. The halide-based technology, which is also compatible with precious-metal recovery from sulfide minerals, also eliminates acid misting and solvent extraction, and it results primarily in the production of by-product elemental sulfur rather than sulfuric acid.

   The halide leaching and electrowinning process has not been adopted by industry due to large capital investment in current smelters, the risk of new technology that has not been proven on a large scale, and the incompatibility with existing electrowinning operations due to the morphology of the deposit, which is granular, rather than smooth using current technology. This project is designed to modify the morphology of the resulting copper deposit to make it compatible with existing electrowinning processes.

8. **Development of Chemical and Biochemical Techniques for the Extraction of Mercury from Fine Coal Particle Solutions. (WV010)**

Principal Investigator: Scott M. Hurst, Anthony G. Abatjoglou and Jay M. Weidermann, West Virginia University
Period of Performance: May 1, 2004- October 31, 2006 (2-Year Project)

The WVU Tech Project, "Development of Chemical and Biochemical Techniques for the Extraction of Mercury from Fine Coal Particle Solutions", includes three objectives: development of a biochemical technique to facilitate the conversion of organically bound forms of mercury to water soluble mercury, development of a chemical technique using physically adsorbed ligands that selectively removes mercury from an aqueous solution that contains relatively large concentrations of other metals, and the development of a biochemical process for extracting liquid mercury from the ligands. The results of this work will be the bases for the development of a novel process for extracting mercury from coal solutions in a "zero waste" manner.

9. Coal Desulfurization with Hypochlorite (WV011)

Principal Investigator: Ray K. Yang & Eung Ha Cho, West Virginia University
Period of Performance: May 1, 2004- October 31, 2006 (2-Year Project)

The utilization of coal as a feedstock to produce carbon materials is very much hampered by the presence of its sulfur content particularly organic sulfur content. However, the organic sulfur is extremely difficult to remove because much of its sulfur atoms are "inserted" into the matrix of the coal structure. Thus, unless the coal structure is "destroyed", the sulfur atoms can not be removed. Chlorine is one of a few chemicals known today that have capability to reduce organic sulfur in a practical sense. However, this chemical chlorinates the coal structure especially at its low pHs, which becomes a roadblock for commercialization of a process utilizing this chemical. We observed through preliminary experiments that hypochlorite has a capability to reduce pyritic sulfur and organic sulfur at high temperatures in a solution. Hypochlorite is the predominant chlorine derivative at high pHs.

This proposal is for continuation of a current project entitled "Coal Desulfurization Using Hypochlorite and Cupric ion As a Catalyst – Feasibility Study," funded by CAST for 2003 – 2004. During the past 6 months, more than 30 experiments were conducted to explore the feasibility of desulfurization of Pittsburgh No. 8 coal with hypochlorite and cupric ammine. It was found that cupric ammine and hypochlorite could not be prepared in the same solution because ammonia used to solubilize cupric reacts with hypochlorite to hydrazine (N 2H 4). It was also found that cupric ammine used in a pretreatment of coal did not catalyze the desulfurization of coal with hypochlorite in the next step. The catalysis is the major theme of the current project.

Thus, a new leaching scheme was used, and a couple of experiments were conducted. The coal was leached with hypochlorite and then the leach coal was hydrolyzed in a sodium hydroxide solution at high temperatures without having a pretreatment step. It was found that this desulfurization method was better than the proposed method which had an additional pretreatment step. The results of an experiment with the new method showed that the total sulfur was reduced from 3% to 1.8% or 40% reduction at 0.68 molar

hypochlorite and 0.2 molar sodium hydroxide at 90 0C. This reduction is translated into 80% reduction of pyritic sulfur and 20% reduction of organic sulfur. The chlorine content of the hydrolyzed coal was 0.6% which is much lower than any other reported values in the literature for chlorine leaching. It is felt that the sulfur reduction could be improved if more rigorous conditions such as higher temperatures above 90 0C (but lower than 100 0C) and higher concentrations of sodium hydroxide above 0.2 molar in the hydrolysis step were applied.

It is proposed in the continuation project that the coal desulfurization process with hypochlorite leaching and then hydrolysis with sodium hydroxide be optimized in terms of particularly hypochlorite concentration and temperature. The optimization will be based on a compromise between maximum sulfur reduction and minimum hypochlorite consumption. High-sulfur coals such as Illinois No. 6 and Upper Freeport coal will be used particularly in the continuation project. The desulfurization behaviors of these coals will be compared to that of Pittsburgh No. 8 coal which will be characterized for the rest of the current desulfurization project.

10. Phyto-Extraction / Fabrication of Gold and Silver Nanoparticles (WV012)

Principal Investigator: Ray K. Yang & Eung Ha Cho, West Virginia University
Period of Performance: May 1, 2004- October 31, 2006 (2-Year Project)

In the traditional cyanidation process, cyanide solutions are used extensively to leach precious metals from crushed ores, concentrates, and enriched tailings. Being extremely poisonous, cyanide solutions are heavily regulated, if not outright banned, in many regions around the world. One of the mid- to long-term research priorities of the Center for Advanced Separation Technologies is to develop such an alternative for precious metal extraction. An emerging alternative with great potential is phytomining i.e., growing plants that hyper-accumulate high concentrations of a target metal. A phytomining operation would entail planting a hyperaccumlator crop over a low-grade ore body or mineralized soil, followed by harvesting and incineration of the biomass to ash to produce “bio-ore”. Phytomining has several advantages over conventional mining. It offers the possibility of utilizing ore bodies or mineralized soils that are otherwise uneconomical, and its effect on the environment is minimal; the area to be mined may be “ready-vegetated”; a “bio-ore” has a higher metal content than a conventional ore and needs far less space for storage. Being in its infancy, phytomining is not yet commercialized, and more research and development are still needed to make this technology cost effective. One way to make its commercialization a reality is to produce products, such as gold nanoparticles which are highly valuable in today’s marketplace and are expected to be in ever increasing demands in the future.

The long-term goal of our phytomining program is to bridge together future mining industry with nanoparticle market via phytomining. This is to be done by re-focusing phytomining at producing, not just gold ingots, but more importantly, gold nanoparticles (crystallite or primary particles measuring less than 100 nm in size) for the rapidly expanding nanoparticle market. This new and re-oriented phytomining, which may gradually start to take shape as a result of successfully conducting the proposed research,

has the potential of becoming a promising method to mass produce gold and other metallic nanoparticles, making the nanoparticles produced by future mining industry competitive in the rapidly expanding nano-product market.

The proposed tasks of this proposal cover a broad front of experimentation in order to eventually achieve the long-term goal envisioned. The experimental studies, due to the exploratory nature of the proposed research, will focus on phyto-extraction/fabrication of gold nanoparticles from hyperaccumulator plants, bean sprouts, and plant cells grown in callus and suspension cultures. The research tasks aim at providing a better understanding of the gold nanoparticles produced by the various plants selected, the external factors that impact the forms and sizes of the nanoparticles produced in those plants, and the fundamental phyto-fabrication processes leading to their formations. One may term the proposed tasks as high risk exploratory research, but even if only one of tasks leads to a profound finding the pay-off could be reasonably high.

11. Recovery of Gold from Thiosulfate Leach Liquor Using Activated Carbon (WV012)
Principal Investigator: Courtney A. Young and Larry G. Twidwell, Montana Tech
Period of Performance: June 1, 2005-October 31, 2006 (2-Year Project)

Gold is generally recovered from the ore by a cyanide leaching process. This procedure is used because of its simplicity and ability to work effectively at low concentrations. However, cyanide itself is highly toxic. Furthermore, it also leaches relatively non-specifically causing other metals to go into solution as well. These metal cyanide complexes can also be toxic. Resulting leach solutions have been accidentally released from various process facilities causing environmental damage. Consequently, particularly over the last decade, alternatives to cyanide leaching have been sought.

Particular attention has been given to thiosulfate; however, recovery of the gold from the thiosulfate leach presents a problem. Conventional carbon adsorption does not work so more expensive recovery processes have been investigated with resin adsorption being the most common. The research we propose to undertake investigates a novel use of activated carbon by pre-adsorbing cuprous cyanide at its surface and using it to exchange with gold in a metal-exchange, cementation-type reaction:

$$Au(S2O3)23- + Cu(CN)2- ads \rightarrow Au(CN)2- ads + Cu(S2O3)23-$$

Resulting cuprous thiosulfate is recycled for further gold leaching with the copper serving as catalyst to the leaching process. Likewise, the adsorbed gold cyanide product can be eluted using a subsequent conventional gold recovery process common in traditional cyanide operations:

$$Au(CN)2- ads + CN- \rightarrow Csite + Au(CN)2- + CN-$$

Consequently, the novel process is believed to be cost-effective and will ultimately allow thiosulfate leaching to be a viable alternative to cyanide. Because direct investigation of these adsorption reactions are masked by the location of the carbon

adsorption sites in commercial activated carbons, we propose to study them in-situ using Raman spectroscopy.

We also propose to investigate using coal-based metathesis technologies to generate carbon alternatives to activated carbon. In this regard, carbon nanotubes, because of their graphite- like structure, is expected to have similar adsorption capacities and could therefore prove to be an extremely effective high surface-area alternative with high adsorptive capacity. Although nanotubes are currently expensive, their production from coal and other cheap carbon sources could be economically equivalent to coconut shell-based activated carbons.

12. The Effect of Alkyl Diphenyl Oxide and Sulfonated Oleic Acid Surfactants on Nucleation and Growth of Potassium Sulfate Crystals: Optimization of Surfactants for the Potash Industry (NM005)

Principal Investigator: Gillian Bond and Christa Hockensmith, New Mexico Tech
Period of Performance: June 1, 2005-October 31, 2006 (2-Year Project)

We have shown that significant improvements occur in the crystal size distribution (CSD) of potassium sulfate crystallized from potassium sulfate/magnesium sulfate brine at 40°C in the presence of concentrations of Calfax 16L-35 {a linear, alkyl diphenyl oxide (ADO) disulfonate surfactant} well below the critical micelle concentration (CMC). The ratio of granular particles to fines is very greatly improved, with essentially all the crystals having sizes between 2 and 3mm. This size range is very desirable for potassium sulfate crystals that will be supplied for agricultural use as a spreadable fertilizer. However, the yield, at present, is too low for commercial application.

We now propose:

To optimize the yield obtainable with ADO disulfonate surfactants, while maintaining the desirable CSD.

To study the performance of sulfonated oleic acid surfactants with a view to improving CSD and yield.

The Carlsbad potash basin accounts for 85% of mined potash production in the United States and it is for the potash industry that this work's goals are set. A successful outcome to this work will benefit a critical industry in New Mexico, and help to ensure the viability of the new potassium sulfate production facility that is under construction near Carlsbad.

13. Thiosulfate as a Replacement for Cyanide in the Presence of Activators

Principal Investigator: Maurice C. Fuerstenau, University of Nevada, Reno
Period of Performance: June 1, 2005-October 31, 2006 (2-Year Project)

The United States is the third largest producer of gold in the world, and Nevada is by far the largest gold-producing state in the country. In processing gold and other precious

metals, cyanide is used universally as a lixiviant. It is effective and reasonably low cost and has been used for greater than a century commercially. It is an extremely toxic reagent, however, and considerable care must be exercised to prevent personal injury and harm to the environment during and after metal processing. To obviate the downsides of the use of cyanide, considerable research has been conducted with other lixiviants that are not as toxic as cyanide to establish if a replacement for cyanide can be found. These include the halides (chlorine, iodine and bromine), thiourea, thiosulfate and polysulfides. Of these reagents thiosulfate is the most promising. The problem with this reagent, however, is the stability of thiosulfate in solution. Oxidative conditions are essential for the dissolution of gold and under these conditions, some thiosulfate is oxidized to tetrathionate, and its effectiveness is greatly reduced. The development of reaction conditions is needed in which the kinetics of gold dissolution is increased, while the losses of thiosulfate by oxidation are minimized. In this investigation the use of activators in gold dissolution will be studied, and the interaction between the various parameters involved in thiosulfate leaching of gold will be carefully investigated.

14. Phytomining for Nickel and Silver Nanoparticles (WV016)

Principal Investigator: Ray K. Yang & Eung Ha Cho, West Virginia University
Period of Performance: June 1, 2005- October 31, 2006 (2-Year Project)

Phytomining is the production of a metal by growing high-biomass plants that hyper-accumulate high concentrations of a target metal. A phytomining operation would entail planting a hyperaccumlator crop over a low-grade ore body or mineralized soil, followed by harvesting and incineration of the biomass to ash to produce “bio-ore”. Some plants are natural hyperaccumulators, while others require induction for hyperaccumulation. Phytomining has several advantages over conventional mining. It offers the possibility of utilizing ore bodies or mineralized soils that are otherwise uneconomical, and its effect on the environment is minimal; the area to be mined may be “ready-vegetated”; a “bio-ore” has a higher metal content than a conventional ore and needs far less space for storage.

The proposed research may eventually be able to bridge together future mining industry with nanoparticle market via phytomining using the nanobiotechnology techniques currently being developed at a fast pace. This may be done by re-focusing phytomming aiming to produce, not just metals, but more importantly, metallic nanoparticles for the rapidly expanding nanoparticle market. The nano-product market, on the other hand, may just as well find that the re-oriented phytomining has the potential of becoming a promising approach to mass produce nickel, silver and other metallic nanoparticles, with advantages similar to that of producing human and veterinary vaccines from plants.

The long-term goal of the proposed research is to tailor-make in large scale and at much reduced costs nickel and silver nanoparticles in the sizes and shapes suitable for use in a variety of industries with high demands for such nanoparticles. Exploratory research tasks, including investigations on nickel and silver nanoparticles in growing plants, as well as silver nanoparticles in bean sprouts and plant cells, will be conducted simultaneously through this two-year project using a scanning probe microscopy, aiming to achieve the following two objectives: (1) to show the existence of nickel and silver

nanoparticles in a few carefully selected species of plants in various forms including their ashes, and (2) to study the sizes, shapes, surface characteristics, and other pertinent features of the nickel and silver nanoparticles formed therein, and investigate the factors that influence their relevant properties.

d) Modeling and Control

1. Online Monitoring and Diagnosing of Coal Fines During Separation Process (WVWV008)

Principal Investigator: B.S. Kang and E.K. Johnson, West Virginia University
Period of Performance: May 1, 2003- October 31, 2006 (2-Year Project)

The goal of this research program is to develop an on-line, non-contact, elemental analysis of coal fines during solid-solid separation process through the use of Laser-Induced Breakdown Spectroscopy (LIBS). Of particular interest is the detection and quantitative measurement of the amount of carbon, sulfur, mercury, and other trace elements in the separated coal fines. The proposed experimental technique will be applied to a circulating fluidized bed (CFB) riser system for determination of coal fines separation efficiency as well as optimization of the separation process variables using a fuzzy logic control approach.

2. Development of a Novel Optical Radiation Depolarization Technique for On-Line Measurements of Particle and Bubble Sizes (KY003)

Principal Investigators: D. Tao, M.P. Menguc and C. Crofcheck, University of Kentucky
Period of Performance: May 1, 2003- October 31, 2006 (2-Year Project)

Grinding and froth flotation are the two most important processes for mineral beneficiation. The importance of grinding is well reflected in the fact that approximately 80% of beneficiation costs are for grinding, mainly due to high energy consumption. To reduce energy consumed by grinding, fines should be removed quickly from the grinding circuit. This requires a reliable on-line particle size analysis technique. Similarly, froth flotation is the most widely used solid-solid separation process for coal and minerals beneficiation and about 90% of mineral concentrates are produced by froth flotation. Air bubble size distribution plays an important role in flotation separation performance but optimization of bubble size distributions will only be possible if bubble size can be monitored on-line.

The proposed project is aimed at developing an optical radiation depolarization technique for on-line size measurement of particle sizes in grinding and bubble sizes in flotation. The technique is based on the analysis of angular and radial profiles of reflection and transmittance of an object subjected to a collimated, polarized light beam. A hybrid Monte Carlo/Ray Tracing method will be used to simulate the depolarization of radiation by particles or air bubbles and size distributions will be determined by best fitting experimentally determined vertical and horizontal polarization components of the radial and angular profiles of reflection and transmission. The proposed technique should

also be able to determine water film thicknesses and bubble separation distance distributions in foams.

3. Mineral Liberation Analysis in 3D by X-Ray MicroCT for the Evaluation of Particle Separation Efficiency. (UT006)

Principal Investigators: C. L. Lin, University of Utah
Period of Performance: May 1, 2004- October 31, 2006 (2-Year Project)

New processing technology for improved productivity and efficiency is the key to success in today's highly competitive market place. It has been well established that appropriate analytical control systems can provide for such improvements. This is especially true of the particle separation processes used in the coal and mineral industries. In general, the separation efficiency for multiphase particulate systems depends on the statistical characteristics of particle microstructures, such as composition distribution, surface exposure of mineral grains, etc. For continued technological progress in the field of multiphase particulate separation processes, the need for quantitative spatial analysis of multiphase particles in three-dimensions has increased significantly. Such quantitative information must be accurate enough so that the measured values can be used as parameters for simulation models, process design procedures, and control strategies. Cone-beam X-ray microtomography technology (XMT) offers a unique imaging capability that can produce high-resolution (a few micrometers) three-dimensional images of the internal structure of multiphase samples. We propose to adapt this new technology to the mining industry to provide for the advanced analysis of coal and ore samples; such analysis of on-line plant samples will allow continuous control of separation processes. In this regard, The primary objective of the proposed project is the development of x-ray micorotomography technology (XMT) for detailed 3D liberation/exposure analysis of coal and mineral samples. The secondary objective will be to evaluate the feasibility of the XMT technology for the control of separation processes. At present, results from traditional sink/float and polished-section analysis cannot be obtained in a reasonable amount of time to provide a satisfactory feedback mechanism for the control of various unit operations in coal preparation and mineral processing plants. This new XMT will combine the high-resolution 3-D XMT instrument and a classification algorithm in order to determine the sample composition and particle characteristics of plant samples. XMT will permit a fast, direct, and detailed 3-D analysis without sample preparation. Reconstruction of 3-D particle populations from XMT images will not only provide sufficient information to construct the true liberation spectrum for the coal and ore samples in question, but also provide information on the particle size distribution, grain size distribution, and exposed surface area of mineral matter grains contained in each particle of the population sample.

Results from the proposed research will improve the efficiency of valuable mineral recovery using direct measurement of liberation information in order to optimize the separation efficiency. The XMT technique will be of great utility for the liberation analysis of a wide variety of mineral resources, including coal, industrial minerals, and metallic ores. In this regard, the XMT technology for coal washability analysis will allow for blending control to maximize coal recovery from coal preparation plants at a specified

product quality. The results from the proposed research can be easily incorporated into existing simulation and estimation software systems for convenient application in industrial practice, both in the coal industry and in the mineral industry. Development of the XMT technology will allow for more rapid, detailed, and accurate analysis than previously thought possible.

4. A Comprehensive Study of Froth Behaviour. (VT011)

Principal Investigators: Roe-Hoan Yoon, Demetri Telionis and Pavlos Vlachos, Virginia Tech

Period of Performance: May 1, 2004- October 31, 2006 (2-Year Project)

Froth flotation is the most widely used and versatile method of separating one solid from another in the coal and minerals industries. In this process, air bubbles are used to selectively collect hydrophobic particles and rise to the surface of a flotation pulp, forming a froth phase. The stability of the froth plays an important role, as it determines the final grade, recovery and throughput. Despite its importance, little is known of the mechanisms involved in the stability of foam and, particularly, of flotation froth, as most of the information available in the literature is on dry foam without particles.

It is, therefore, proposed to conduct a comprehensive study on both dry and wet foams in the presence of particles. The proposed work will include determination of bubble size distribution, particle size distribution, liquid fraction (or air-hold-up), grade of hydrophobic particles along the heights of froth columns. The results will give information on the effects of both hydrodynamic and surface chemistry parameters on froth stability. The new information obtained in the present work will be used to develop a froth model. It will be combined with the model describing the bubble-particle interactions occurring in the pulp phase, so that a comprehensive flotation model will be developed. Since the combined model will be based on first principles, it will have predictive and diagnostic capabilities, and can be used for developing methods of improving flotation. The basic information obtained in the present work will be particularly useful for developing effective deformers, maximizing carrying capacity, and improving coarse particle flotation.

5. Portable Sensor for Detecting Mercury and other Heavy Metals Encountered in Coal Processing and Utilization (WV013)

Principal Investigators: A. Manivannan and Mohindar S. Seehra, West Virginia University

Period of Performance: May 1, 2004- October 31, 2006 (2-Year Project)

A two year research program is proposed to develop a portable and reliable sensor for on-site detection of mercury in solutions in the ppb range using boron-doped diamond (BDD) electrodes. This proposal is based on our demonstrated feasibility of detecting mercury in laboratory solutions in the ppb range using the BDD electrodes. Similar success has been accomplished for detecting Pb, Cd, and Cu in solutions. For mercury detection, the media used so far have been KCl, and KNO 3. Proposed research include developing the necessary calibration curves for Hg in other media such as thiocyante

(KSCN), perchlorate, and EDTA, the use of a rotating disk electrode to improve sensitivity and reproducibility of results, and testing of the flue gas samples obtained from coal-fired plant at NETL (Pittsburgh). The tasks needed to develop a suitable portable unit are appropriately addressed. Feasibilty of similar portable system for detecting other heavy metal ions encountered in coal processing and utilization is described.

e) Environmental Control

1. Electrolytic Solution Purification and Metal Recovery from Metal-Bearing Toxic Waste Streams (UT003)

Principal Investigator: Michael L. Free, University of Utah
Period of Performance: May 1, 2003- October 31, 2006 (1-Year Project)

Industry creates numerous waste streams, many of which contain dissolved metal ions that must be removed to preserve the environment. Many of these waste streams can be created by natural processes that are accelerated by industry such as acid mine drainage, made as byproducts of chemical processing such as metal extraction, or as the result of manufacturing processes such as electronic component manufacturing. Often such wastes are complex and involve multiple metal ions. Regardless of the waste origin, toxic metal ions must be removed.

In the proposed project a novel method of removing multiple toxic metals from aqueous media by selective pulse-plating with high surface area electrodes will be evaluated and developed in a manner that will allow the metals to be recovered individually as purified metals in an environmentally sound way. The direct production of metal as a byproduct, rather than as a toxic waste, will contribute to better resource utilization as well as a reduction in toxic waste generation.

2. Determining the Effectiveness of Gold Filters for Removing Mercury from Coal Fired Power Plants (MT003)

Principal Investigator: K. Ganesan, Montana Tech
Period of Performance: May 1, 2003- October 31, 2006 (1-Year Project)

Because the US EPA is planning to regulate mercury emissions from power plants, there is a clear need to develop devices that can cost effectively remove mercury from power plant flue gases. Most current research has focused on transferring mercury from the air stream to fly ash or converting elemental mercury to divalent mercury to absorb it in wet scrubbers. However, when low chlorine content coal is combusted most of the mercury in the flue gas exists as elemental mercury, which is very hard to remove. Thus, to comply with the potential 90% mercury reduction proposed by EPA, one must oxidize the elemental mercury to either mercuric chloride or oxide as a way to collect particulates. In either case, mercury is merely converted to a form that is also difficult and expensive to recover. Therefore, it appears that directly removing mercury from the flue gas will be the most cost effective and environmentally friendly approach. This proposal is focused on removing elemental mercury from flue gas using gold filters. The

main objective of this research is to evaluate the effectiveness of gold wire mesh in removing mercury vapor from flue gas. A wire mesh made of thin (<0.1 mm diameter) gold wires will be tested in the laboratory, initially with a synthetic gas stream containing mercury vapor in the range of 1-300 $\mu g/m^3$. Similar tests will be conducted in combustion gases by burning six types of western and eastern coals. The study will be conducted for six concentration levels of mercury; 5, 10, 25, 50, 100 and 300 $\mu g/m^3$.

3. Development of Metallic Filters to Control Mercury From Coal Fired Power Plant Flue Gas (MT004)

Principal Investigator: K. Ganesan, Montana Tech
Period of Performance: May 1, 2004- October 31, 2006 (1-Year Project)

The focus of this research is to develop metallic filters to remove vapor phase mercury from coal fired flue gas. Three types of metallic filters will be tested for its effectiveness in removing mercury vapor from gas streams. Based on the results, one of them will be tested for its performance in a flue gas stream of a coal fired power plant. The previous funding from CAST enabled the PI to investigate the potential of gold filters to remove mercury vapor from gas streams. The results indicate that the removal efficiency is over 90% with gold filters. In addition, preliminary tests with silver filters showed promising results. Therefore, this proposal is to test three metallic filters: copper wire with gold plating, copper wire with silver plating and copper wire mesh. These filters initially will be made in the laboratory and tests will be performed to compare their performance. Tests will be performed at concentration ranges of 1-100 μg/m3 of vapor phase mercury. Tests also will be performed at elevated temperatures by heating the incoming air stream up to 250ºF. Two bench scale systems will be designed based on the results of the laboratory and field study. These filters then will be tested in the field in a coal fired power plant flue gas stream. This field work will be conducted in collaboration with PPL Montana, in Colstrip where four coal fired power plants are in operation. The results of this field tests will provide valuable information of the performance of these filters in real world conditions. The data then will be used to design a pilot scale system for further testing.

4. Recovery of Chromium and Arsenic From Toxic Waste Streams by Reactive Polymer-Coated Absorbents (WV014)

Principal Investigators: Dianchen Gang & Baolin Deng, West Virginia University
Period of Performance: May 1, 2004- October 31, 2006 (2-Year Project)

One of the major challenges facing coal and metal mining industries today is to address public concerns of environmental damage associated with the mining activities. Oxidation of pyrites and other metal sulfides in coal and metal mine tailings can generate high concentration of sulfuric acid, forming acid mine drainage (AMD) that may contain high concentrations of sulfate, iron, and many toxic elements suc h as arsenic (As) and chromium (Cr). The objective of this project is to develop a novel method of removing and recovering As and Cr from wastewater including AMD. Reactive polymers will be synthesized under defined conditions and their structure be optimized according to their capability for As and Cr removal and recovery. This study focuses on these anionic

contaminants (i.e., AsO 4 3-/AsO 3 3- and CrO 4 2-) because they are highly soluble and normally not removed by many of the treatment processes designed for divalent heavy metals such as lime neutralization and precipitation. The research objective is consistent with the research roadmap developed by CAST on the chemical separations and environmental control issues. The development and successful testing of this material could potentially lead to a patent application.

5. **Determination of Factors Affecting the Separation of Potentially Hazardous Trace Elements and their Behavior in Coal Tailings Impoundments (KY005)**

Principal Investigators: Frank E. Huggins, Naresh Ahah, Gerald P. Huffman, University of Kentucky

Period of Performance: June 1, 2005- October 31, 2006 (2-Year Project)

A number of trace elements in coal are of significant environmental concern. Such potentially hazardous elements include As, Cr, Se, and Hg, and are regulated under either the 1990 Clean Air Act Amendments or the 1976 Resource Conservation and Recovery Act or both. Coal cleaning is performed principally to minimize the amount of pyrite and other mineral matter entering pulverized coal combustion. At the same time, hazardous trace elements associated with these minerals are also removed from coal combustion and hence their environmental impact during combustion is thereby reduced. However, such trace elements tend to be concentrated in the waste tailings from coal separation technologies, which normally are disposed of under water in coal waste impoundments. Here, trace elements may pose other environmental problems because both major and trace elements may be leached and mobilized. Consequently, the waters in such impoundments have to be isolated from the local groundwater in order to avoid possible contamination of local drinking water supplies. Despite concerns about solubilized trace elements in coal impoundments, relatively little is known about the concentrations and specific chemical forms of such trace elements that can be leached from coal minerals and mobilized in these waters. More data are clearly needed to assess the environmental hazard from mobilized ions in coal tailings impoundments.

The behavior of trace elements in both coal separation technologies and tailings disposal scenarios depends on their modes of occurrence and associations with major minerals or macerals in the coal or coal fractions. Such information is rarely determined, but is of vital importance to our understanding of trace elements in these processes. In this proposal, we intend to determine the mineral or chemical forms (mode of occurrence) and association of a number of critical trace elements (As, Cr, Se, Hg, etc.) in coals and coal fractions using a comprehensive array of conventional and advanced characterization methods. Our intention is to collaborate with other CAST-supported investigations of advanced coal separation technologies that can supply the clean coal and tailings fractions needed for this investigation. The information obtained will then be used (i) to determine the efficiency of various coal cleaning methods for specific trace element removal; (ii) to interpret the behavior of specific elemental forms and associations in coal tailings exposed to water in laboratory simulations of storage ponds;

and (iii) to assess the actual environmental impact posed by specific trace elements in coal tailings impoundments.

6. **Mercury Reduction From Coal Power Plant Emission Using Functionalized Ordered Mesoporous Carbons (FOMCs) (WV015)**
   Principal Investigators: Dianchen Gang & Baolin Deng, West Virginia University
   Period of Performance: June 1, 2005- October 31, 2006 (2-Year Project)

   One of the major challenges facing coal-fired power plants (CFPPs) today is to address the public concerns of mercury emissions. Mercury emitted from CFPPs exists in two valence states: elemental mercury (Hg0) and oxidized forms (Hg2+). Elemental mercury is normally dominant, accounting for 92% to 99% of the total mercury in the flue gas. The effectiveness of an individual control technology for Hg emission depends largely on its chemical speciation. For example, Hg0 is highly volatile with low water solubility, therefore, it is not absorbed significantly by water-based scrubbing processes. The objective of this project is to develop and evaluate functionalized ordered mesoporous carbons (FOMCs) for the maximum Hg removal from flue gas emissions at high temperature (80 – 200oC). Highly ordered mesoporous carbons (OMCs) with uniform nanopore size will be synthesized under defined conditions and their structure optimized according to their capability toward Hg removal in the high particulate environment. OMCs will be functionalized by elemental sulfur and other chemicals to enhance Hg uptake. The research objective is consistent with the research roadmap developed by CAST on the chemical separations and environmental control issues. The development and successful testing of this material could potentially lead to a patent application.

7. **Removal of Metal Ions from Acid Mine Drainage using a Novel Low-Cost, Low Technology (WV017)**
   Principal Investigators: Benjamin Dawson-Andoh, West Virginia University
   Period of Performance: June 1, 2005- October 31, 2006 (2-Year Project)

   Acid Mine Drainage (AMD) produced by active and dormant coal mines continues to pose a major threat to the environment. One of the goals of the National Energy Policy developed by President Bush in 2001 is “to ensure the steady supply of affordable energy in environmentally responsible and sustaining manner.” Current technologies employed to remove toxic environmental polluting metals from AMD are expensive and economically challenging to the Coal Mining Industry. The work proposed here seeks to evaluate a low-cost, low technology that employs renewable biomaterials: wood and fungal biomass, to remove toxic metals that occur in AMD. Additionally, the proposed work also seeks to determine the recovery potential of toxic metals from the biomaterials and the regeneration and re-use of the biomaterials. West Virginia is one of the premier hardwood States in the US and tremendous amount of wood biomass is available as residue. The proposed study if successful will provide an avenue for the use of the tremendous wood biomass generated by both the primary and secondary forestry operations in West Virginia.

EXPERIMENTAL

The CAST initiative is comprised of a diverse group of subprojects, most of which are multistage, task-oriented developmental projects that cannot be conveniently categorized by the traditional reporting criteria required by the DOE Uniform Reporting Requirements. For example, several of the projects have required the construction of unique test equipment, others the generation of simulation models, etc., as preliminary tasks in the overall execution of the project. As such, they are more appropriately described and discussed as "Project Tasks" within the context of the individual Technical Progress Reports. These reports are attached to this document as Appendices and should be referred to for this information.

RESULTS AND DISCUSSION

The CAST initiative is comprised of a diverse group of subprojects, most of which are multistage, task-oriented developmental projects that cannot be conveniently categorized by the traditional reporting criteria required by the DOE Uniform Reporting Requirements. For example, several of the projects have required the construction of unique test equipment, others the generation of simulation models, etc., as preliminary tasks in the overall execution of the project. As such, the presentation of results is more appropriately described and discussed within the context of the individual Technical Progress Reports. These reports are attached to this document as Appendices and should be referred to for this information.

CONCLUSIONS

There are currently forty six (46) sub-projects being funded of which nineteen (19) are completed and final reports will be issued.. A six-month Progress Report (covering the period April 1, 2006-September 30, 2006) for the active projects was generated for each of these sub-projects and has been attached to this document as an Appendix. A brief summary of progress during thereportin period, along with plans for the future on each of the sub-projects is given below.

a) Solid-Solid Separation

1. Development of Novel Ultrafine Sizing Methods. (Joint UK/VT Project) (KY001/VA008)

Principal Investigators: R.-H. Yoon and G.H. Luttrell, Virginia Tech
Principal Investigators: R.Q. Honaker and BK. Parekh, University of Kentucky
Period of Performance: May 1, 2003-October 31, 2006 (2-Year Project)

Project work was continued during the past reporting period to investigate a variety of techniques for high efficiency sizing of ultrafine particles. Much of the work conducted to date focused on improving the performance of classifying cyclone system with a new water injection apex. This effort included (i) installation of automatic sampling system and testing of a new water injection system, (ii) preprocessor work for Computational Fluid Dynamics (CFD) analysis using GAMBIT v 2.0 software (i.e. geometry construction and meshing generation). The test work conducted to date indicates that a new water injection apex substantially reduces the amount of ultrafine solids that are bypassed to the coarse fraction without increasing the particle cutsize.

Work will continue to evaluate the classification performance of the hydrocyclone equipped with the water injection apex. Furthermore, a wide variety of theoretical studies will be continued in an attempt to develop a better understanding of the problems associated with ultrafine particle sizing. These studies will include computational fluid dynamics (CFD) application to predict classifier performance.

2. Dispersion and Flotation of Clays from New Mexico Potash Ores. (NM001)

Principal Investigators: I. Gundiler, S. Titkov, and M. Yekeler, New Mexico Tech
Period of Performance: May 1, 2003- October 31, 2006 (1-Year Project)

Very high clay potash ores, which heretofore could not be processed with the existing technologies, can be economically treated with combined mechanical and flotation desliming followed by potash flotation. At the same level of slime depressant and amine collector consumptions, potash recovery has increased by 20% with two stage mechanical desliming followed by slime flotation. Reversing the order of slime flotation reagents, i.e., flocculant and slime collector, reagent consumptions decreased drastically, at the same time decreasing KCl loses to the slimes. Addition of inorganic dispersants, such as

aluminum sulfate to the first stage coarse desliming also improves desliming efficiency as reported in the previous progress reports.

In light of these observations, screening tests conducted with the commercially available slime flotation collectors, oxyethylated fatty acids and fatty amines, as reported for low and medium clay ores in the previous reports, have been reexamined. Preliminary observations confirm the above conclusions that by reversing the order of flocculant and slime collector addition into the pulp, the reagent consumptions and KCl loses to slimes can be reduced drastically. These results will be presented in the final report.

3. Flotation Technology for the Trona Industry. (UT001)
Principal Investigator: Jan D. Miller, University of Utah
Period of Performance: May 1, 2003- October 31, 2006 (2-Year Project)

The project is complete and a final report is to be issued.

4. Flotation Processes/Experiments and Analysis. (VT009)
Principal Investigators: D. Telionis and P. Vlachos, Virginia Tech
Period of Performance: May 1, 2003- October 31, 2006 (2-Year Project)

The project is complete and a final report is to be issued.

5. Column Flotation of Relative Coarse and Fine Dolomitic Phosphate Pebbles. (WV007)
Principal Investigator: Felicia F. Peng, West Virginia University
Period of Performance: May 1, 2003- October 31, 2006 (2-Year Project)

In this reporting period we focused on the studies of pH effect on the dolomite flotation and interaction of dissolved spices effect on the depletion of collector, in the real dolomitic phosphate ore flotation, and compared with the published theoretical pure dolomite and francolite mineral flotation system. The details of the findings are reported.

The work will continue on the characterization of new dolomitic phosphate pebble sample C, and prepare for relatively coarse particle flotation. The slime effect and particle size effect on the dolomite-phosphate separation performance will be continued to measure. The sample C will be further prepared for relative coarse particle batch flotation to determine the reagent conditions. The flotation column modification and testing for relative coarse particle flotation will also continued.

6. Beneficiation of Mixed Potash Ores From New Mexico. (NM004)
Principal Investigator: Ibrahim Gundiler, Lynn Brandvold, Tanja Pietraß, Stanislav Titkov, New Mexico Tech
Period of Performance: May 1, 2004- October 31, 2006 (2-Year Project)

Sylvite-langbeinite mixed ore, high-grade langbeinite ore, high-kieserite langbeinite ore samples, langbeinite gravity concentrates and kieserite concentrates were collected,

analyzed and mineralogical compositions were determined. Samples were prepared and a series of flotation tests were carried out with long and short chain fatty acids, fatty amines, sulfates, and sulfonates. So far, flotation of sulfate minerals was achieved only with fatty acid collectors. NMR studies to better understand soluble salt flotation were initiated along with zeta potential measurements in dilute brines as a function of pH.

Micro-flotation tests using relatively pure mineral samples are currently being carried out using commercially available reagents. An attempt is being made to synthesize the reagents suggested in the literature for selective separation of langbeinite and kieserite, or used in the past kieserite or langbeinite flotation operations. Fundamental studies will also be continued with Mg bearing minerals.

7. Development of New Reagents for the Flotation of Dolomite from Phosphate Ore. (NV002)

Principal Investigators: Maurice C. Fuerstenau, Manoranjan Misra and Thomas W. Bell, University of Nevada, Reno
Period of Performance: May 1, 2004- October 31, 2006 (2-Year Project)

Various analogs of betaine and sarcosine were tested as flotation collectors in a microflotation cell. None of the betaines displayed notable potential. The sarcosine analogs show strong flotation collector properties for apatite and dolomite. Electrokinetic determinations in conjunction with flotation experiments indicate that sarcosine adsorbs on dolomite by two mechanisms depending on pH. Below the pzc, sarcosine would appear to be adsorbing physically on the surface. Above the pzc, chemisorption is apparently occurring.

Future work will involve testing the various sarcosines on a phosphate ore containing about 15 wt % dolomite. Infrared experiments will be conducted to establish mechanisms of collector adsorption to establish optimal conditions for flotation.

8. High Frequency Eddy Current Separation of Metallic Residue from Slags, Sands, Electronic Scrap and Other Wastes. (UT004)

Principal Investigators: Raj K. Rajamani, University of Utah
Period of Performance: May 1, October 31, 2006 (2-Year Project)

The project is complete and a final report is to be issued.

9. Dry Particle Separation in a CFB Riser System. (WV009) (Continuation from CAST 1)

Principal Investigator: Eric Johnson and Bruce W. Kang, West Virginia University
Period of Performance: May 1, 2004- October 31, 2006 (2-Year Project)

The project is complete and a final report is to be issued.

10. Studies of Froth Stability and Model Development. (VA002)

(Continuation from CAST I)

Principal Investigator: Roe-Hoan Yoon, Virginia Tech
Period of Performance: May 1, 2004-May 31, 2006 (2-Year Project)

Continuation of this project is funded under CAST III. A final report for CAST II is being prepared.

11. Direct Measurement of Forces in Flotation. (VA004)
(Continuation from CAST I)
Principal Investigator: Roe-Hoan Yoon, Virginia Tech
Period of Performance: May 1, 2004- October 31, 2006 (2-Year Project)

Continuation of this project is funded under CAST III. A final report for CAST II is being prepared.

12. Enhanced Flotation Performance Through Column Froth Enrichment (KY006)
Principal Investigators: Rick Q. Honaker and Daniel Tao, University of Kentucky
Period of Performance: June 1, 2005-May 31, 2005 (2-Year Project)

The accomplishments achieved to date can be summarized as follows:
A graduate research assistant, Mr. Carlos Munoz, has been hired to work on the project as part of his M.S. degree requirements. Mr. Munoz has worked for four years as a Mining Engineer in the copper industry in Chile. However, he had very little flotation experience. As such, a significant amount of time has been devoted to providing knowledge and training in flotation fundamentals and column operation.

A commercially available magnetic plastic called 'PolyMag' has been secured in large quantities. Contact angle measurements revealed excellent surface hydrophobicity with an angle of 83o, which is larger than generally realized for most coal and mineral surfaces. Also, the material is easily ground to the required particle size using a hammer mill.

Two run-of-mine coal samples have been collected and crushed to the required particle size for the flotation tests, i.e., -65 mesh. The sources include the Hazard No. 4 coal seam and the Pittsburgh No. 8 coal seam. It is expected that selective detachment using the magnetic plastic material or external recycling may be more beneficial for coal in the rejection of sulfur, which is found at high concentrations in the Pittsburgh No. 8 coal seam.

Preliminary tests have not provided evidence that the injection of the magnetic plastic or the application of ultrasonic energy into the froth zone improves flotation selectivity on the basis of ash rejection. A more fundamental approach to the test program is needed to evaluate the potential impact and to quantify the potential improvement. Improved sulfur rejection has not been addressed to date but the process samples are currently being analyzed to assess the potential.

Future work will include obtaining carrying capacity limit for the Pittsburgh # 8 sample, run several test at carrying capacity limits with adding magnetic plastic material at

different solid concentration rate into the froth zone. Recover the magnetic plastic material with a magnetic separator and evaluate the impact of adding higher hydrophobic material into the froth zone for ash and total sulfur rejection.

Repeat the same test describe above by using the same clean coal obtained at different feed rates instead of plastic material to quantify the impact of adding the plastic.

Collect a pure coal by obtaining 1.3 float material and pure coal pyrite by gravity separation. Conduct flotation tests on each component separately and as a blend with and without the magnetic plastic material using varying concentration amounts. The effort in the tests will be to quantify the amount of selective detachment that occurs under different solid loadings and quantities of magnetic plastic material.

13. Engineering Development of a Fine Particle Heavy Medium Separator (VA012)

Principal Investigators: Gerald H. Luttrell, Virginia Tech and Robert Moorhead, Krebs Engineers, Inc

Period of Performance: June 1, 2005-October 31, 2006 (2-Year Project)

Initial work has begun to design, fabricate and construct a prototype heavy medium cyclone specifically designed for treating fine coal. The work completed to date includes shipping of the necessary components from Krebs Engineers to the Virginia Tech test facility, assembly of these parts with components fabricated at Virginia Tech, and the initial setup of the associated pilot-scale circuitry necessary to evaluate the new technology. A preliminary test plan has also been developed for future testing of the prototype separator.

Future work will focus on the completion of construction activities and initiation of preliminary shakedown tests for the prototype heavy medium cyclone.

14. Improved Destruction and Control of Residual Flotation Froths (VA014)

Principal Investigators: Gerald H. Luttrell and Roe-Hoan Yoon, Virginia Tech

Period of Performance: June 1, 2005-October 31, 2006 (2-Year Project)

During this reporting period, frother partitioning studies and froth evaluation tests were conducted at an industrial plant site. The frother partitioning studies indicate that the samples must be taken in the field to avoid frother decomposition and/or adsorption on coal particles that interfere with the measurements. Preliminary results from the froth evacuation tests indicate that direct evacuation is not by itself capable of deaerating coal flotation froths. Modifications have been made to the test apparatus in an attempt to improve this technique.

During the next reporting period, plant water will be analyzed with the new approach described above for its frother content (surface tension measurements), size distribution, combustibles and ash content and, chemical composition. Froth stability tests will also be carried out to develop a better understanding of the effects of particles size and frother content on froth stability. A modified froth evacuation system will also be

examined in more detail.

15. **Development of a Turbulent Flotation Model and a Computer Simulator (VA015)**
Principal Investigators: Roe-Hoan Yoon and Gerald H. Luttrell, Virginia Tech
Period of Performance: June 1, 2005-October 31, 2006 (2-Year Project)

. An analytical drainage model has been derived that incorporates liquid flow through both the PBs and PB junctions. Applied a simple boundary and initial conditions, the simulation results on this model showed that drainage is more likely to occur through PBs when the foam is wet, while it is through vertices with dry foams. The findings by this model may be useful in controlling the stability of foams and froths hence the productivity of related natural resources.

Future work will be done conducted with more realistic boundary conditions (such as coagulations and foam growing) and various initial conditions (free drainage or forced drainage) accompanied by some experimental validations. In addition, associating the effects by particles and surfactants in any manner will also be necessary for an advanced model. Another, the contribution of liquid films in drainage is controversial but may be accountable in the future work. Then the complete drainage model will be able to be combined into the flotation model.

16. **Novel Surfactants as Collectors for Froth Flotation (VA017)**
Principal Investigators: Richard D. Gandour, Virginia Tech
Period of Performance: June 1, 2005-October 31, 2006 (1-Year Project)

We made twelve new compounds that have been fully characterized. The lowest member of the series is R1 = C6H13; this means that the two-tail amphiphile has 13 carbons in 4(1+n2) and 13 carbons in 5(1+n2). Additional members of the 4(1+n2) series have 15, 17, 19, and 21 carbons, respectively; those of the 5(1+n2) series have 17, 19, 21, 23, and 25 carbons, respectively. Using the methods develop for the series, we modified the hydroxyl end-group of polymers. These modified polymers bound to iron nanoparticles more strongly than oleic acid; the unmodified polymer did not bind to the nanoparticles.

17. **Alternative materials for Dense Medium Separation (KY004)**
Principal Investigator: Rick Honaker, University of Kentucky
Period of Performance: June 1, 2005-October 31, 2007 (2-Year Project)

During this reporting period, fine sand was used to obtain a preliminary assessment of the ability to use plant fine waste material to form an adequate dense medium in coal cleaning applications. The separation performances achieved when cleaning ¼-in x 28 mesh Coalberg coal were compared with those obtained using commercial grade B magnetite. The investigation was performed using a 15-cm (6-in) diameter dense medium cyclone in a closed-loop circuit. The findings can be summarized as follows:

a. The stability of the sand suspension was significantly better than that provided by the reference magnetite of a broad range of medium densities and feed inlet pressures.

b. As expected, medium stability substantially improved with an increase in medium density and a decrease in feed inlet pressure. Stability is a function of particle population which determines the degree of hindered settling and the total system particle surface area which ultimately affects medium viscosity.
c. In general, the density offsets were lower with the sand-based medium as opposed to the reference magnetite suspension, which is likely due to better medium stability.
d. At a 1.5 RD, the sand-based medium provided an excellent separation performance as indicated by an organic efficiency of nearly 98%.
e. Viscosity effects apparently hampered separation performance at a 1.6 RD as indicated by a drop in recovery with an increase in product ash content. The organic efficiency decreased to about 94%.
f. The probable error values obtained for the sand-based medium were approximately 60% higher than those achieved using the reference magnetite.

As a result of the positive separation performances, flotation column tailings will be recovered from an operating preparation plant and tested as a magnetite alternative during the next reporting period.

Activities in the following areas were also realized during the current reporting period:

a. Steel slag samples were obtained from Stein, Inc who specializes in steel scrap processing. The steel slag for crushed to -100 mesh using a cage mill. The material will be evaluated in the dense medium circuit.
b. Another steel production waste material known as 'C' waste will also be evaluated. Reportedly, 'C' waste contains more iron and, thus, should be more magnetic. The quantity of 'C' steel waste in the U.S. is in the millions of tons.
c. Work is on-going to recover magnetic material from combustion fly ash using a spiral and magnetic separator.

Future work will include:

a. Evaluate the separation performance efficiency data generated from the use of the flotation reject.
b. Complete the evaluation of the coarse magnetite material for high-density separations.
c. Initiate work on the evaluation of the steel production waste sources.
d. Analyze the rheological properties of the various mediums.

18. Measurement of Surface Forces Between Hydrophobic Surfaces

Principal Investigators: Roe-Hoan Yoon, Virginia Tech
Period of Performance: June 1, 2005-October 31, 2007 (2-Year Project)

During the current reporting period, CV, contact angle and surface force measurements were used to study the adsorption of amyl xanthate on gold, and the hydrophobic force between hydrophobic xanthate layer surfaces. The CV test verified the chemiadsorption of amyl xanthate on gold. The contact angle and surface force measurements revealed the

reverse orientation phenomena of amyl xanthate on gold surface. According to the surface force measurement, the attractive hydrophobic force which is much greater in magnitude and range than expected for the van der waals force between hydrocarbon surfaces has been detected at the high water contact angles.

Much of the work conducted during the next reporting period will focus on the surface force measurements between the ZnS surfaces.

b) Solid-Liquid Separation

1. Improving Densification of Fine Coal Refuse Slurries to Eliminate Slurry Ponds. (KY002)
Principal Investigators: B.K. Parekh and R.Q. Honaker, University of Kentucky
Period of Performance: May 1, 2003- October 31, 2006 (2-Year Project)

The project is complete and a final report is to be issued.

2. Development and Testing of a Horizontal Pressure Belt Filter. (VA010)
Principal Investigators: R.-H. Yoon & G.H. Luttrell, Virginia Tech
Period of Performance: May 1, 2003- October 31, 2007 (2-Year Project)

During the latest project period, construction and assembly of the major components of the pressure belt filter where completed. The pressure vessel was shipped to a fabrication and welding shop to have two sight glasses installed, to check all of the welds for safety reasons, and to manufacture two end plates for the vessel. Also, the fabrication shop performed a hydrostatic test on the completed vessel and determined that vessel is structurally sound. All of the electrical and pressure vessel safety checks have been completed. Shakedown testing is now underway (i) to complete the performance testing all of the major components, (ii) to test their operational effectiveness of the unit, and (iii) to remedy any design weaknesses that may be identified.

Work during the next reporting period will continue to include some fabrication and assembly activities as required based on the results obtained from the shakedown tests. This work will be followed by a detailed test program and economic evaluation. The detailed test program will include a study of key operating variables including feed flow rate, feed solids content, feed size distribution, filter belt speed, filter cloth mesh size, and applied pressure.

3. Development of a Fine Particle Centrifuge. (VA006)
(Continuation from CAST I)
Principal Investigators: G.H. Luttrell & R.-H. Yoon, Virginia Tech
Period of Performance: May 1, 2004- October 31, 2007 (2-Year Project)

During this reporting period, construction of a continuous unit was continued and the problem in the mechanical water seal was eliminated. Several series of shakedown tests

were carried out in batch mode. The data indicate that the moisture reduction is significantly better at higher rotation speeds and with the injection of air. However, the capabilities of the prototype cannot be fully established until additional tests are completed with the unit operating in continuous mode. This mode of operation required the integration of a thickening unit into the test circuitry. This modification makes it possible to improve fines recovery by circulating fines previously lost through the screen back to the circuit feed.

Future work will involve any improvements necessary to achieve a stable process. Once proven, detailed tests will be run to fully evaluate the capabilities of the unit for a variety of coal samples and over a wide range of operating conditions.

4. **Improvements in Screen Bowl Centrifuge Performance. (VA013)**
   Principal Investigators: Robert C. Bratton & G.H. Luttrell, Virginia Tech
   Period of Performance: May 1, 2004- October 31, 2007 (2-Year Project)

   Field tests conducted in the present work again demonstrate that flocculant injection can be used to effectively reduce the solids content of main effluent that is discarded by a screen-bowl centrifuge. The in-plant tests indicate that both reagent dosage and type is important in obtaining the best overall results. The test data also suggest that the moisture content of the screen-bowl product may increase slightly due to the recovery of fine particles displaced from the main effluent. For the tests conducted to date, the data suggest that the increase in moisture is only about 2 percentage points.

   During the next reporting period, test work will again focus on the characterization of full-scale screen-bowl centrifuge performance at an industrial site. The tests are to be performed as a function of key operating variables (i.e., feed slurry flow rate and solids content).

c) Chemical/Biological Extraction

1. **Bio-Assisted Heap Leaching of Nickel Laterites for the Development of a Domestic Nickel Industry. (UT002)**
   Principal Investigator: S. Duyvesteyn, University of Utah
   Period of Performance: May 1, 2003- October 31, 2006 (2-Year Project)

   This project is completed and a final report is to be issued.

2. **The Development and Utilization of Alkaline Sulfide Leaching and Recovery of Gold. (MT001)**
   Principal Investigator: C. Anderson and L.G. Twidwell, Montana Tech
   Period of Performance: May 1, 2003- October 31, 2006 (2-Year Project)

   The project is complete and a final report is to be issued.

3. **Hydrometallurgical Processing of Chalcopyrite Concentrates. (NV001)**

Principal Investigator: M. Misra and M. Fuerstenau, University of Nevada, Reno
Period of Performance: May 1, 2003- October 31, 2006 (2-Year Project)

The project has been completed and a final report will be issued.

4. **Simultaneous Electrolysis of Copper and Ferrous Ions to Produce Copper Cathode and to Regenerate Ferric Sulfate - The Lixiviant to Dissolve Copper Sulfide Minerals. (MT002)**
Principal Investigator: C. Young, H.-H. Huang and C. Fabian, Montana Tech
Period of Performance: May 1, 2003- October 31, 2006 (2-Year Project)

The project is complete and a final report is to be issued.

5. **Ion Exchange Recovery of Cobalt from Copper Leach Solutions. (NM002)**
Principal Investigator: I. Gundiler and M. Hatch, New Mexico Tech
Period of Performance: May 1, 2003- October 31, 2006 (2-Year Project)

Small particle size picolylated diethylenetriamine ion exchange resins tested in small columns at slow and moderately fast flow rates for absorption of cobalt and copper at very low concentrations (10, 16ppm Co2+; 25, 40ppm Cu2+) in a pH 2.1 copper raffinate solution showed that capacity for absorbing cobalt increased on CHEL-40 resin over that found in our earlier fast flow tests. However, the slow flow rates had little or no effect on the capacity for absorbing copper. Our newly synthesized picolylated diethylenetriamine resin CHEL-73 (which was slightly less picolylated than the CHEL-40 resin) absorbed cobalt at moderately high flow rates as well as did a lesser volume of CHEL-40 at a slow flow rate.

Comparison tests were made with the commercially available hydroxypropyl picolylamine resin and dipicolylamine resin ground to similar particle sizes. Our new picolylated polyamine resin (CHEL-40) showed the best comparative capacity for cobalt, copper and nickel, and desirably, the least Fe3+ capacity in the column absorption tests at fast flow rates. Both our new resins performed better than the commercially available resins, especially for cobalt absorption capacity from the pH 2.1 mining raffinate. When 200 bed volumes of the raffinate solution was passed at high flow rates on a small bed of the best performing new resin (CHEL-40), significant amounts of cobalt and nickel were absorbed on the resin along with only a minor amounts of iron from the raffinate. The absorbed cobalt (along with nickel, iron and zinc) could be eluted easily from the resins by using water and 0.1M H2SO4. The absorbed copper required 1M H2SO4 solutions for effective elution.

Elution with 0.5- 2M H2SO4 of both the CHEL-40 and CHEL-73 resins which were loaded with appropriate volumes of raffinate feed yielded main eluate fractions whose cobalt concentration was over 10 times, and the copper concentration of over 50 times those present in the raffinate feed solutions.

Although these enrichment ratios are well within the conventional ion exchange separation guidelines, utilization of these resins ion the copper mining industry for the intended purpose is not very likely at this time due to low absorption capacity for cobalt and the high cost of picolylamine based resins. However, these resins could find ready applications in other industries, such as electro-plating and cobalt refining for purification of mother liquors from copper and nickel. Currently industrial partners are being sought for commercializing these resins and potential patent applications are being considered.

6. **The Effect of Diphenyl Oxide Surfactants on Nucleation and Growth of Potassium Sulfate Crystals: Development of Enhanced Surfactants for the Potash Industry. (NM003)**
   Principal Investigator: G. Bond and C. Hockensmith, New Mexico Tech
   Period of Performance: May 1, 2003- October 31, 2006 (2-Year Project)

   The project is complete and a final report is to be issued.

7. **Overcoming Technological Barriers to More Efficient Recovery of Copper from Chalcopyrite. (UT005)**
   Principal Investigator: Michael L. Free, University of Utah
   Period of Performance: May 1, 2004- October 31, 2006 (2-Year Project)

   The project is complete and a final report is to be issued.

8. **Development of Chemical and Biochemical Techniques for the Extraction of Mercury from Fine Coal Particle Solutions. (WV010)**
   Principal Investigator: Scott M. Hurst, Anthony G. Abatjoglou and Jay M. Weidermann, West Virginia University
   Period of Performance: May 1, 2004- October 31, 2006 (2-Year Project)

   The project is complete and a final report is to be issued.

9. **Coal Desulfurization with Hypochlorite. (WV011)**
   Principal Investigator: Ray K. Yang & Eung Ha Cho, West Virginia University
   Period of Performance: May 1, 2004-May 31, 2006 (2-Year Project)

   The project is complete and a final report is to be issued.

10. **Phyto-Extraction / Fabrication of Gold and Silver Nanoparticles. (WV012)**
    Principal Investigator: Ray K. Yang & Eung Ha Cho, West Virginia University
    Period of Performance: May 1, 2004-May 31, 2006 (2-Year Project)

    Gold nanoparticles were produced from the leaf extracts of three cultivars of geranium. The bio-formation process appears to be very rapid, achieving high concentrations of gold nanoparticles in about 35 to 60 minutes. The nanoparticles produced were found to remain stable for several months. The intra-cellular contents of gold in the cells of carrot, periwinkle, and stevia in suspension cultures and in the sprouts

of mung bean and alfalfa are noticeably enhanced, overall, as the gold concentrations in contact with the plant cells or the sprouts increase, confirming the extraction and transportation of gold ions into the cells of the plants tested. In addition, the contents of gold in cells cultivated in suspension cultures are, in general, much more than several-fold higher compared to that in sprouts. This indicates the potential of using suspension culture of plant cells for large scale production of gold nanoparticles.

11. Recovery of Gold from Thiosulfate Leach Liquor Using Activated Carbon (MT005)

Principal Investigator: Courtney A. Young and Larry G. Twidwell, Montana Tech
Period of Performance: June 1, 2005-October 31, 2006 (2-Year Project)

A novel carbon adsorption technology for extracting gold from thiosulfate solutions was examined. Unless pretreated, activated carbons will not adsorb gold thiosulfate. However, by first adsorbing copper cyanide onto the carbon, gold thiosulfate was adsorbed in an ion-exchange reaction. Copper cyanide was adsorbed at pH 10.5 and was found to yield higher adsorption densities than at pH 11. The difference was attributed to solution speciation. When the Cu-pretreated carbon was placed in gold thiosulfate solutions, 100% gold extraction was observed as long as enough copper on the carbon was present. Gold-to-copper ratios of 1:1 were observed at pH 10.5 for all concentrations; however, at pH 11, ratios of 1:1 were observed only at low concentrations. Higher concentrations yielded a ratio of 0.6:1. Differences can also be attributed to solution speciation but may also have been caused by differences in researchers, experimental procedures, and activated carbons as discovered during this latest research campaign. Clearly, the envisioned process works but needs considerable work to characterize as well as optimize.

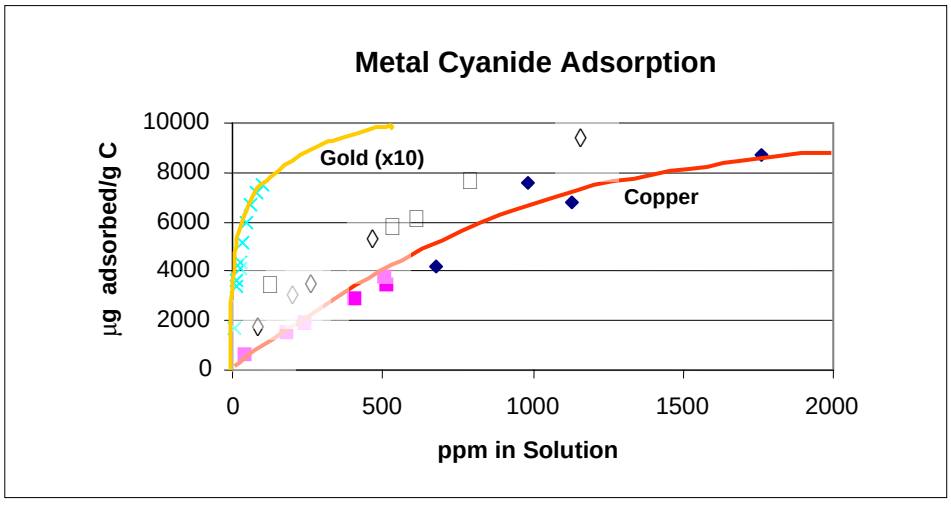

Figure 1. Adsorption isotherms on carbon for copper cyanide compared to literature for gold cyanide (Marsden and House, 2006). Closed symbols are preliminary data conducted at pH

11 for the proposal (Young and Twidwell, 2005) and open symbols are current data conducted at pH 10.5 for the project.

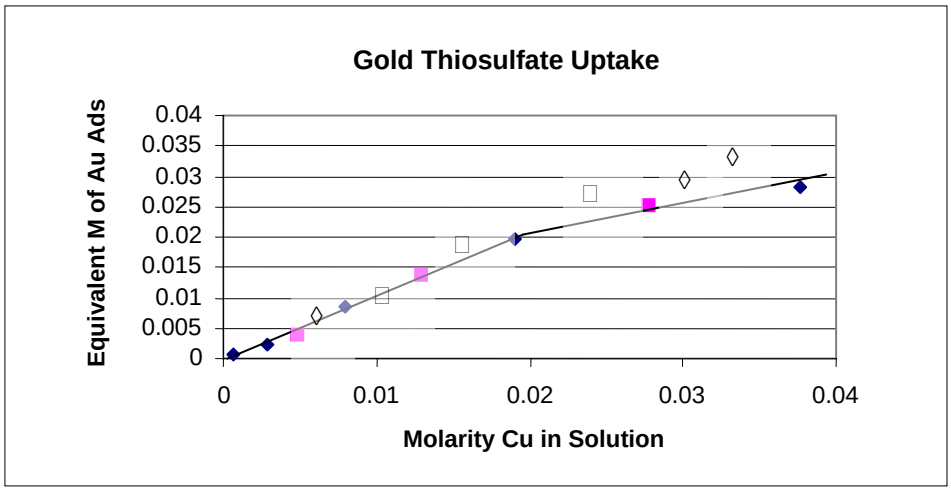

Figure 2. Gold uptake from thiosulfate solutions by copper-activated carbon as a function of copper displaced. Closed symbols are preliminary data conducted for the proposal (Young and Twidwell, 2005) using carbon pretreated with 4700 ppm Cu. Open symbols are current data conducted for the project using activated carbon pretreated with 6000 ppm Cu.

With Task 1 essentially complete except for ongoing library search activities, Task 2 is expected to be completed next; however, due to the lack of adsorption in the current experiments, Task 2 may take longer than anticipated but should be completed by the next reporting cycle with the effect of pH and temperature being examined in detail. Other parameters will also be examined to see if their effects on the process are also critical such that a factorial design experiments will be conducted to model and optimize the process using StatEase software. This will then allow Task 3 to commence along with Task 6. Task 3 may be completed by the next reporting cycle; however, Task 6 will not. Task 3 involves maximizing gold adsorption and therefore will likely follow StatEase testing as well. Task 6 will commence next summer with Dr. Greg Hope at Griffith University in Australia by the graduate student via a subcontract. Arrangements for his visit are being made at this time. Tasks 4 and 5 will commence then as well but will not be examined in detail until the student returns from the trip.

12. The Effect of Alkyl Diphenyl Oxide and Sulfonated Oleic Acid Surfactants on Nucleation and Growth of Potassium Sulfate Crystals: Optimization of Surfactants for the Potash Industry (NM005)

Principal Investigator: Gillian Bond and Christa Hockensmith, New Mexico Tech
Period of Performance: June 1, 2005-October 31, 2006 (2-Year Project)

The project is complete and a final report is to be issued.

13. Thiosulfate as a Replacement for Cyanide in the Presence of Activators (NV003)
Principal Investigator: Maurice C. Fuerstenau, University of Nevada, Reno
Period of Performance: June 1, 2005-October 31, 2006 (2-Year Project)

These studies have shown that cupric ion concentration is the most important factor in this system. Concentrations of ammonia and thiosulfate are also important, since ammonia controls the concentration of free cupric ion in solution, and thiosulfate controls the rate of reaction. Kinetic parameters of cupric ion reduction were established. Results show that the reduction rate increases when thiosulfate concentration increases and temperature is elevated. Experiments also show that higher concentrations of thiosulfate are necessary for gold leaching at room temperature than at higher temperature. An electrochemical cell has been constructed for measuring thiosulfate concentration in the presence of cupric ion.

Future work will concentrate on optimizing concentrations of cupric ions, ammonium thiosulfate, and ammonia for gold leaching. The effect of additives will also be investigated.

15. Phytomining for Nickel and Silver Nanoparticles (WV016)
Principal Investigator: Ray K. Yang & Eung Ha Cho, West Virginia University
Period of Performance: June 1, 2005- October 31, 2006 (2-Year Project)

Silver nanoparticles were produced from the leave extracts of three cultivars of geranium. The bio-formation process was found to be rapid, achieving high concentrations of silver nanoparticles in about 15 to 24 hours. Light was required for the bio-reactions involved, while exposure to oxygen appeared to have no significant effect. The nanoparticles produced were found to remain stable for several months. The intra-cellular contents of silver in stevia cells cultivated in suspension cultures and in the sprouts of mung bean and alfalfa are noticeably enhanced, overall, as the silver concentrations in contact with the plant cells or the sprouts increase, confirming the extraction and transportation of silver ions into the cells of the plants tested. In addition, the contents of silver in cells cultivated in suspension cultures are, in general, higher compared to that in sprouts.

Future experimental work to be conducted include: (1) To continue our investigation on the extra-cellular formation of silver nanoparticles by geranium; (2) To grow nickel-hyperaccumulator plants, *Alyssum murale Waldst & Kit* (or *Alyssum murale*), *Alyssum corsicum Duby* (or *Alyssum corsicum*), and *Alyssum bertolonii,* and study the nickel nanoparticles formed in those plants; (3) To initiate and develop callus cultures of geranium and *Alyssum spp*.; the former has just been started; (4) To continue and expand our investigation on intracellular formation of silver nanoparticles in suspension cultures of geranium, *Alyssum spp.,* stevia (both hairy root and cell), beet, and periwinkle; and (5) To continue our investigation on silver nanoparticles formed in the sprouts of mung bean and alfalfa.

d) Modeling and Control

1. **Online Monitoring and Diagnosing of Coal Fines During Separation Process. (WV008)**
   Principal Investigator: B.S. Kang and E.K. Johnson, West Virginia University
   Period of Performance: May 1, 2003- October 31, 2006 (2-Year Project)

   A dynamic LIBS system has been developed to detect C, Fe, and Hg in coal. Significant information has been obtained in analyzing the signals. Based on qualitative and semi-quantitative analysis, dynamic LIBS testing provides basic information on the lifetime and temporal characteristics for individual emission lines. Our test results (as reported earlier in the previous progress report) showed that Mercury seems to have a more sudden decay, while carbon and iron show a slight delay before actual decay occurs. The data upon observation of emission lines of one specie compared to another suggests that emission lines posses differing temporal characteristics.

   The sensitivity and accuracy of the LIBS method developed within the scope of this research can be improved upon. This research has shown that all of the elements of interest have the possibility of being quantitatively analyzed much faster than the traditional ASTM methods. Because of the limited detection of mercury and sulfur within the synthetic coal mixtures, future work should be focused on the development of the sensitivity limits and the synchronization of the current LIBS system.

   Because of the effects of oxygen quenching mercury and sulfur emission lines, a vacuum environment or an inert gas environment could be created to enhance LIBS signals. To further enhance the signal, the CCD detector could be replaced by an Intensified CCD (ICCD) camera. An ICCD camera with time gating capabilities can be up to one thousand times more sensitive than a regular CCD camera. If the ICCD camera is used as a detector, and the samples are placed in a vacuum environment, the current LIBS apparatus could attain sensitivity in the part per billion range.

   Dynamic LIBS testing gives us qualitative data of how different emission lines behave. The analysis of the dynamic LIBS signals allowed for observations of time-dependent characteristics of different emission lines. Because the system was not synchronized, a "brute force" method was relied upon to obtain usable dynamic LIBS signals. Synchronization of the spinning mirror in conjunction with the laser and the CCD camera would be necessary for commercialization of this apparatus. Anomalies in the dynamic LIBS data were observed. A further study of these anomalies will allow for a better understanding of the temporal behavior of the emission lines and the laser-induced plasma.

2. **Development of a Novel Optical Radiation Depolarization Technique for On-Line Measurements of Particle and Bubble Sizes. (KY003)**
   Principal Investigators: D. Tao, M.P. Menguc and C. Crofcheck, University of Kentucky
   Period of Performance: May 1, 2003- October 31, 2006 (2-Year Project)

   The project is complete and a final report is to be issued.

3. **Mineral Liberation Analysis in 3D by X-Ray MicroCT for the Evaluation of Particle Separation Efficiency. (UT006)**
   Principal Investigators: C. L. Lin, University of Utah
   Period of Performance: May 1, 2004- October 31, 2006 (2-Year Project)

   The project is complete and a final report is to be issued..

4. **A Comprehensive Study of Froth Behaviour. (VA011)**
   Principal Investigators: Roe-Hoan Yoon, Demetri Telionis and Pavlos Vlachos, Virginia Tech
   Period of Performance: May 1, 2004- October 31, 2006 (2-Year Project)

   The CAST II component of this project has been completed and a final report is in preparation.

5. **Portable Sensor for Detecting Mercury andother Heavy Metals Encountered in Coal Processing and Utilization. (WV013)**
   Principal Investigators: Mohindar S. Seehra, West Virginia University
   Period of Performance: May 1, 2004- October 31, 2006 (2-Year Project)

   The problem of the "reproducibility" of the calibration curves for Hg detection using the same BDD electrode was investigated. A peak due to copper impurity from the gold solution used in the detection was discovered. It is suggested that in the electrode cleaning process, stripping in the range of -0.4 V to 1.0 V may result in a clean electrode for subsequent measurements. Copper or silver solution may also be used instead of the gold solution for capturing mercury in an amalgam. These experiments will be carried out in the near future.
   We plan to focus on the following issues in the near future using the information noted above. First, the voltage range for stripping during the electrode cleaning process will be extended to -0.4 V to +1.0 V covering the peak positions of copper, mercury and gold. This will be followed by repeating the calibration curves to determine their reproducibility. Second, we have placed orders for copper and silver solutions. Each of these will be tried replacing gold solution in the detection of mercury to determine if these offer significant advantages. Finally, results from the above experiments will be used to extend measurements to the PalmSens portable unit for realizing a portable detector. During these experiments, the issue of using standard addition method vs. internal standard method will also be looked into.

6. **Development of a 3D Lattice-Boltzmann Model for Fluid Flow Simulation under Partially-Saturated Conditions in Packed Particle Beds (UT007)**
   Principal Investigators: J Miller and Sukop, University of Utah
   Period of Performance: May 1, 2004- October 31, 2007 (2-Year Project)

   The project is complete and a final report is to be issued.

e) Environmental Control

1. **Electrolytic Solution Purification and Metal Recovery from Metal-Bearing Toxic Waste Streams. (UT003)**
   Principal Investigator: Michael L. Free, University of Utah
   Period of Performance: May 1, 2003- October 31, 2007 (1-Year Project)

   The project is complete and a final report is to be issued.

2. **Determining the Effectiveness of Gold Filters for Removing Mercury from Coal Fired Power Plants. (MT003)**
   Principal Investigator: K. Ganesan, Montana Tech
   Period of Performance: May 1, 2003- October 31, 2007(1-Year Project)

   This project is complete and a final report is to be issued

3. **Development of Metallic Filters to Control Mercury From Coal Fired Power Plant Flue Gas. (MT004)**
   Principal Investigator: K. Ganesan, Montana Tech
   Period of Performance: May 1, 2004- October 31, 2007 (1-Year Project)

   In summary during this reporting period a laboratory scale in-house plating setup was established to fulfill our plating needs. A newer sponge with higher surface area was successfully plated and tested for mercury removal efficiency. The removal efficiency of the newly plated sponge was lower than expected. Perhaps the new sponge is not coated enough for high performance. Therefore to enhance the metal coating, plating time will be increased to improve the thickness of plating. This is currently being attempted.

   Future work will include continuing on optimizing the plating thickness in the sponge based filters to obtain the expected efficiency at a reasonable cost. In addition, a novel bio-nano-sponge will be made in the laboratory and plated with metals. This will be our second generation filters for mercury removal from gas streams. These bio-nano-sponges will be tested for their effectiveness with and without metallic coating. We believe that these new materials can remove mercury even without any additional metallic plating as in other filter mediums.

4. **Recovery of Chromium and Arsenic From Toxic Waste Streams by Reactive Polymer-Coated Absorbents. (WV014)**
   Principal Investigators: Dianchen Gang & Baolin Deng, West Virginia University
   Period of Performance: May 1, 2004-May 31, 2007 (2-Year Project)

   In the past six months, all components in tasks 1 to 3 are finished. Adsorption experiments demonstrated that iron-chitosan can be used to remove arsenic from aqueous solution. The adsorption isotherm fitted Freundlich model well and the maximum adsorption removal efficiency was observed at pH = 9.1. Kinetic batch experiments results indicated that about 60% of the arsenic was adsorbed by the iron-chitosan within the first 30 min and pseudo-second-order model fitted the experimental data well. Effect

of anions on arsenic removal studies showed that competition in multi-sorbate systems could significantly restrain arsenic adsorption, especially if silicate ion is present. Sulfate has only a minimal effect, while phosphate reduces adsorption considerably at pH values greater than 7 where anion adsorption sites are limited. Column studies showed that the breakthrough point was at 768 empty bed volumes (EBV) when flow rate was 25 ml/hr.

In the next reporting period, the project will be finished. The efforts will include: (1) Write final report (2) Prepare paper for publishing.

5. Determination of Factors Affecting the Separation of Potentially Hazardous Trace Elements and their Behavior in Coal Tailings Impoundments (KY005)

Principal Investigators: Frank E. Huggins, Naresh Ahah, Gerald P. Huffman, University of Kentucky

Period of Performance: June 1, 2005- October 31, 2007 (2-Year Project)

During the latest reporting period, we have concentrated on obtaining and evaluating analytical data for the four fractions of the Illinois coal obtained from the Peabody Gateway Preparation Plant, Illinois. A minor problem with the preparation of epoxy mounts, however, has prevented us from obtaining mineralogical data by CCSEM. Owing to negative results from the TCLP leaching protocol, new batch leaching equipment has been constructed for long-term testing of the leachability of trace elements from the tailings fractions and is currently undergoing final testing.

Over the next six months, we should complete our analyses of the Illinois coal fractions and be in a position to evaluate the role and importance of the form of occurrence in determining the behavior of key elements in float/sink separation technologies. In addition, long-term leaching experiments will commence on the two reject fractions to assess the relationship of elemental forms of occurrence to their leachability. We also intend to initiate additional studies with the Illinois coal using different coal separation technologies.

6. Mercury Reduction From Coal Power Plant Emission Using Functionalized Ordered Mesoporous Carbons (FOMCs) (WV015)

Principal Investigators: Dianchen Gang & Baolin Deng, West Virginia University

Period of Performance: June 1, 2005- October 31, 2007 (2-Year Project)

We have tried several approaches to functionalize the surfaces with sulfur and amine functional groups that are expected to have strong affinity for mercury adsorption. Sample characterizations with FTIR, XRD, and TEM have been applied, which have confirmed the success of some functionalization procedures.

We will continue the work with surface functionalization with various functional groups such as amine, sulfur, iodine, and chlorine, and assess how these surface modifications will affect Hg removal efficiency.

7. **Removal of Metal Ions from Acid Mine Drainage using a Novel Low-Cost, Low Technology (WV017)**
   Principal Investigators: Benjamin Dawson-Andoh, West Virginia University
   Period of Performance: June 1, 2005- October 31, 2006 (2-Year Project)

   A major piece of analytical equipment is expected to be installed in November, 2006 and look forward to have some results at the next report period.

   Future studies will focus on the effect of wood species on removal of metal ions, the effect of fungal hyphae of removal of metal ions and the kinetics of metal adsorption by wood.

REFERENCES

References utilized by the individual sub-projects are reported in the relevant Technical Progress Report in the attached Appendices.

Appendix 1: Development of Novel Ultrafine Sizing Methods

(KY001/VA008)

TECHNICAL PROGRESS REPORT

Contract Title and Number:	Period of Performance:
Establishment of the Center for Advanced Separation Technologies (DE-FC26-01NT41091)	Starting Date: 10/1/2002 Ending Date: 10/31/2006

Sub-Recipient Project Title: Development Of Novel Ultrafine Sizing Methods	Report Information: Type: Semi-Annual Number: 6 Period: 10/1/05-3/31/06
Principal Investigators: Roe-Hoan Yoon and Gerald H. Luttrell	Date: 4/30/06 Code: VA008
Contact Address: 146 Holden Hall Virginia Tech, Blacksburg, VA 24061	Contact Information: Phone: (540) 231-4508 Fax: (540) 231-3948 E-Mail: cast@vt.edu
Subcontractor Address: No subcontracts issued.	Subcontractor Information: Phone: Fax: E-Mail:

ABSTRACT

The objective of this project is to develop a broad base of new equipment and improved methods for fine particle sizing. The processes evaluated in this work include a wide variety of mechanical, hydraulic, and novel approaches. For each process, experimental test programs have been undertaken to optimize operating parameters so that maximum efficiency and throughput capacity can be achieved while maintaining particle size cuts in the 25-50 μm size range. The resultant test data has been used to mathematically simulate different circuit arrangements for the most promising technologies. Due to the large scope of this project, the proposed work has been carried out as a joint effort between researchers at the University of Kentucky and Virginia Tech. During this reporting period, an automatic proportional sampling system was constructed for the hydrocyclone test circuit used to evaluate a novel water injection system. The goal of this work is to simultaneously reduce particle size cut point (D_{50}) and bypass using the new water injection apex. Also, geometry construction and mesh generation associated with Computational Fluid Dynamics (CFD) were also carried out during this period for the water injection apex.

INTRODUCTION

Background

Most mineral and coal processing plants are forced to size their particulate streams in order to maximize the efficiency of their unit operations. These sizing techniques commonly include various types of screens and classifiers. Screens exploit differences in the physical dimensions of particles by allowing fines to pass through a perforated plate or open mesh while coarser solids are retained. Unfortunately, screening systems are generally limited to particle size separations coarser than approximately 250μm due to limitations associated with capacity and blinding. Hydraulic classifiers are generally employed for finer size separations, including both static and centrifugal devices. Hydraulic classifiers exploit differences in the settling rates of particles and are influenced by factors such as particle shape and density as well as particle size. Classifiers are generally considered to be more practical than screens for fine sizing, but the separation efficiency decreases dramatically for particles smaller than approximately 150μm (Heiskanen, 1993). In addition, classifiers commonly suffer from bypass, which occurs when a portion of the ultrafine particles (slimes) are misplaced by hydraulic carryover into the oversize product. The unwanted misplacement can have a large adverse impact on downstream separation processes.

Objective and Approach

The development of efficient techniques for fine particle sizing is widely considered to be a high research priority by both the mineral processing and coal preparation industries. In particular, the development of new screening and classification technologies, or improvements on existing technologies, is needed to overcome the current shortcoming of existing processes for fine particle sizing. Therefore, the primary objective of this project is to develop a broad base of new sizing equipment or techniques that can be used to efficiently size ultrafine particles. Processes to be evaluated in the proposed work will include a wide array of mechanical, hydraulic, and novel approaches for fine particle sizing. Because of the inherent difficulties and large scope of work associated with this problem, the research program is being carried out as a joint research program between researchers at Virginia Tech and the University of Kentucky. During this reporting period, much of the project work focused on the evaluation of techniques for improving the performance of classifying cyclone circuits. This effort included (i) installation of automatic sampling system and testing of a new water injection system, (ii) preprocessor work for Computational Fluid Dynamics (CFD) analysis using GAMBIT v 2.0 software, i.e. geometry construction and meshing generation.

PROJECT TASKS

Task 1 - Development of Mechanical Sizing Methods

No additional test work was conducted under this particular task during the past reporting period.

Task 2 – Development of Hydraulic Sizing Methods

No additional test work was conducted under this particular task during the past reporting period.

Task 3 – Development of Novel Sizing Methods

No additional test work was conducted under this particular task during the past reporting period.

Task 4 – Circuit Development and Evaluation

Work under this task has focused on reducing bypass through the application of a novel water injection apex system. Existing water injection systems tend to substantially increase the particle cut size, which makes it unacceptable for ultrafine sizing applications. In addition, existing systems typically require large amounts of clarified injection water that may not be readily available in industrial plants. In light of these problems, technical personnel from Krebs Engineers have worked with the project team to develop a new type of water injected cyclone. The new system is specifically designed to overcome some of the inherent limitations associated with existing apex washing systems. To evaluate this new technology, a proprietary prototype was provided to the project team for initial testing. The experimental test program required the construction of a complete closed-loop test circuit. The circuit, which is designed to be extremely flexible, incorporates a 6-inch diameter classifying cyclone with interchangeable components, an electronically controlled variable speed circulation pump, and an integrated linear-pass proportional sample cutter. During this reporting period, the sample cutter was modified with an automatic pneumatic sampling system to accurately control the amount of samples collected (see Figure 1).

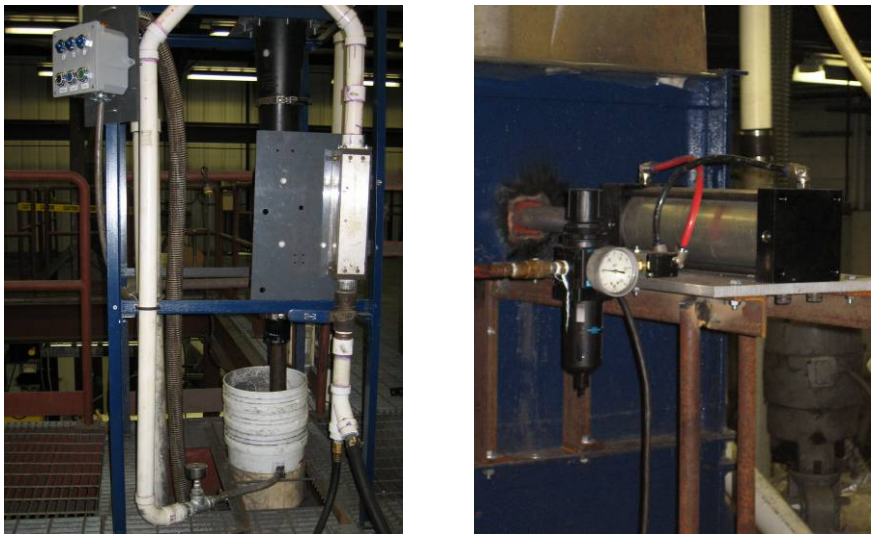

Figure 1. Water injection system and automatic pneumatic sampling system.

Several test runs were conducted during this reporting period to evaluate the effects of water injection pressure and volumetric flow rate. Experiments were carried out using water and minus 100 mesh coal slurry having a solids content of approximately 6.7% solids. The pressure drop across a cyclone was measured by taking the difference between the feed pressure and the overflow pressure. The test data given in Figure 1 show that the new apex washing system provides a higher volumetric throughput and a finer particle cut size at a lower pressure drop, independent of the size of the vortex finder. In fact, a larger vortex finder results in a lower pressure drop for the same volume flow or a greater capacity for the same pressure drop. Conversely, a smaller diameter vortex finder results in a larger pressure drop for the same volume flow. An increase in cyclone pressure usually leads to a higher volumetric throughput and a finer particle cut size (L. Svarovsky, 1984). Several tests for new water injection apex, compared with other apexes, was conducted to demonstrate the improved performance of the water injection apex on particle size cut point (D_{50}) and bypass using a 1.5 inch vortex finder and 120 gpm volumetric flow rate. The data plotted in Figure 2 shows that the new water injection apex has the lowest bypass and particle size cut (D_{50}).

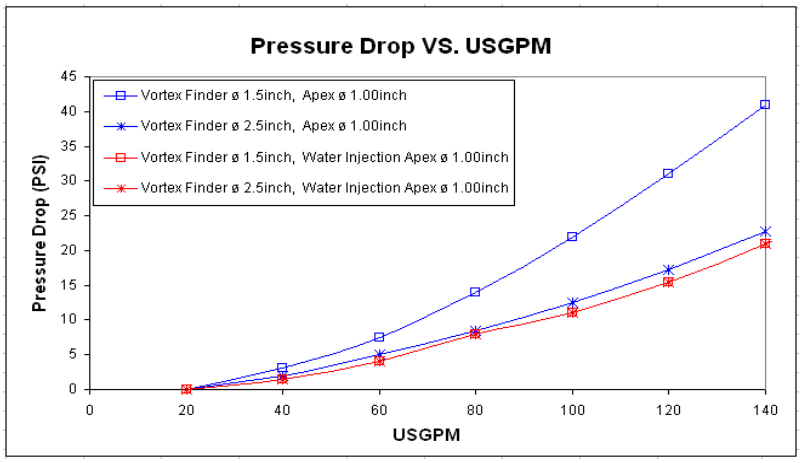

Figure 1. Effect of water injection apex on pressure drop and volumetric flow rate.

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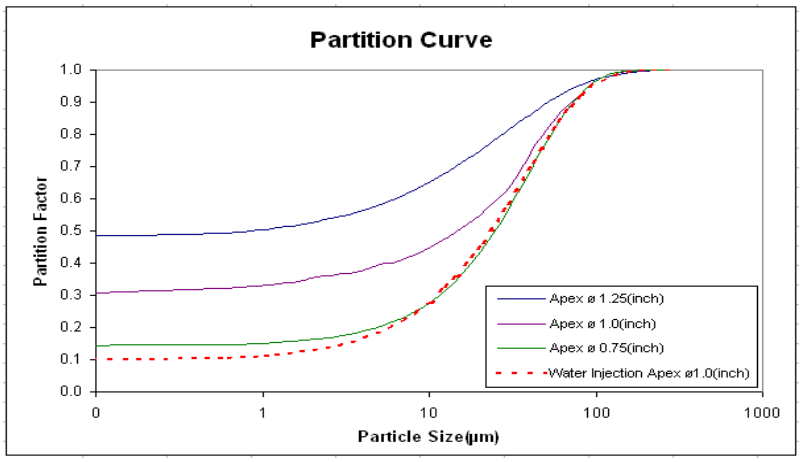

Figure 2. Effect of water injection apex on particle size cut point (D_{50}) and bypass.

Theoretical studies of the new water injection apex were also undertaken during this reporting period using Computational Fluid Dynamics (CFD). This work was performed to investigate the phenomenon which occurs inside the hydrocyclone (i.e., prediction of air core locations, particle trajectory and velocity contours, etc.). During this reporting period, geometry construction and meshing for an actual 6-inch diameter cyclone was generated using the GAMBIT Ver. 2.0 software, which is a single integrated preprocessor for CFD analysis. Figure 3 shows a meshed cyclone equipped with the water injection apex. The mesh consists of 5773 nodes, 2902 mixed wall faces, 12,172 mixed interior faces and 4,763 mixed cells. Several simulations for investigating phenomenon of cyclone with water injection system are expected to be performed during the next reporting period.

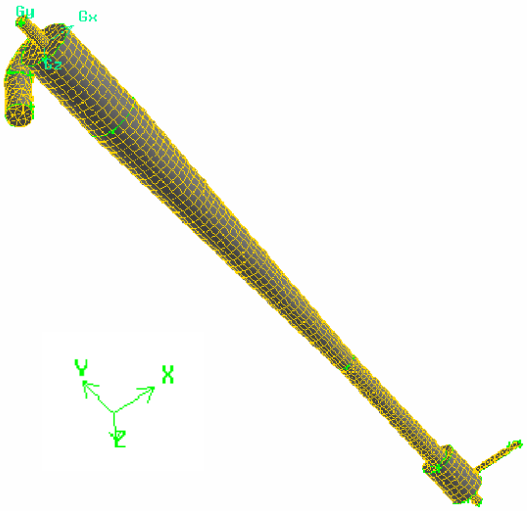

Figure 3. Geometry construction and mesh generation for a hydrocyclone equipped with a water injection apex.

SUMMARY

Project work was continued during the past reporting period to investigate a variety of techniques for high efficiency sizing of ultrafine particles. Much of the work conducted to date focused on improving the performance of classifying cyclone system with a new water injection apex. This effort included (i) installation of automatic sampling system and testing of a new water injection system, (ii) preprocessor work for Computational Fluid Dynamics (CFD) analysis using GAMBIT v 2.0 software (i.e. geometry construction and meshing generation). The test work conducted to date indicates that a new water injection apex substantially reduces the amount of ultrafine solids that are bypassed to the coarse fraction without increasing the particle cutsize.

FUTURE WORK

Work will continue to evaluate the classification performance of the hydrocyclone equipped with the water injection apex. Furthermore, a wide variety of theoretical studies will be continued in an attempt to develop a better understanding of the problems associated with ultrafine particle sizing. These studies will include computational fluid dynamics (CFD) application to predict classifier performance.

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1. Heiskanen K, Particle Classification, Chapman & Hall, 1993.
2. Gambit v2.0 manual, Fluent Inc. 2002

PUBLICATIONS/PRESENTATIONS

None for the current reporting period.

Appendix 2: Dispersion and Flotation of Clays from New Mexico Potash Ores (NM001)

TECHNICAL PROGRESS REPORT

Contract Title and Number:	Period of Performance:
Crosscutting Technology Development at the Center for Advanced Separation Technologies (DE-FC26-02NT41607)	Starting Date: 10/1/2002 Ending Date: 10/31/2007

Sub-Recipient Project Title:	Report Information:
Dispersion and Flotation of Clays from New Mexico Potash Ores	Type: Semi-Annual Number: 7 Period: 04/01/06-9/30/06
Principal Investigators:	Date: 09/06/06
Gundiler, Titkov, Yekeler	Code: NM001-R06
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"No subcontracts issued."	Phone: Fax: E-Mail:

ABSTRACT

The effects of inorganic dispersants, and slime flotation with oxyethylated collectors for desliming high-clay potash ores have been investigated. Both slime dispersants and slime flotation have increased the overall IR recovery into the slimes fraction, decreased K_2O losses into slimes, and decreased IR in desliming tailings (flotation feed). At the same level of flotation reagents consumption, K_2O recovery increased and the concentrate quality improved. It has been shown that incorporating slime flotation into the ore desliming scheme for potash flotation from high-clay ores, which could not be processed with the existing mechanical desliming methods, can successfully be exploited.

INTRODUCTION

Background

New Mexico is the largest potash producer in the United States, supplying the majority of the domestic production. Flotation is the main beneficiation method for sylvinite (KCl-NaCl) ores for the recovery of sylvite (KCl), carried out in saturated brines

with cationic collectors (long chain primary amines). Clay minerals present in the ore also absorb flotation reagents, hence clays are dispersed during grinding and in attrition scrubbers; slimes are then removed by hydrocyclones and hydroseparators from sylvite flotation feed. Elevated brine temperatures during the summer months also affect collector adsorption on clays, depressing sylvite flotation.

Inorganic compounds, such as sodium silicate and poly-phosphates, have been utilized as dispersants for clay minerals in a number of flotation systems. However, in high ionic strength brines the surface charge on clay minerals is practically nil due to double layer compression. Inorganic clay dispersants added in the grinding circuit not only augment slime dispersion but also increase the selectivity of liberation of sylvite-halite mixed grains. Dispersant action of inorganic polyvalent salts, such as aluminum sulfate ($Al_2(SO_4)_3$), have been postulated to be due to recharging of the clay particle surfaces in the presence of polyvalent ions.

Objectives and Approach

This study was initiated to investigate possible means of improving sylvite recovery from Carlsbad potash ores by improving the mechanical desliming processes in the existing plants, and explore more efficient means of slime removal by the use of slime dispersants and/or flotation of slimes ahead of sylvite flotation. Studies on high - clay ores are reported here.

PROJECT TASKS

Task 1 – Materials and Methods

In this phase of the study, the effects of aluminum sulfate as slime dispersant, and slime flotation using oxyethylated fatty acids or fatty amines were investigated with high clay (~11% I.R.) ore samples collected from Carlsbad potash operations. Minus 8 mm ore samples were scrubbed with or without the addition of dispersant for 5 minutes at 50%, solids at 600 rpm. Coarse ore was then diluted to 16% solids and deslimed by siphon decantation (stage-1), ground in a laboratory rod mill to minus 14 mesh (1.18 mm), diluted and again deslimed (stage-2). High-clay ores were deslimed 3 or 4 times as needed. Slimes were filtered, dried, and analyzed for insoluble residue (I.R.) and K_2O content, sands were placed in a flotation cell, conditioned with flotation reagents and sylvite was floated. Concentrates and tailings were also filtered, dried, and analyzed for I.R. and K_2O content.

Task 2 – Desliming and Potash Flotation Test Results

In conventional slime flotation the fines are first agglomerated with a polymeric flocculant, then slime collectors are added and the fines are floated. A similar procedure was followed in our studies as reported for low and medium clay ores. During the course of this investigation, however, it was observed that slimes floated equally well or better when the order of addition of reagents was reversed. Actually, this procedure resulted in

lower reagent consumption and reduced KCl loses to slimes, thus increasing overall potash recoveries in the concentrates.

Base line for potash flotation recovery was established by 3-stage desliming the ore as described above, followed by flotation tests with increasing slime depressant (guar gum) at constant amine collector concentrations.

Figure-1 shows comparison of 3-stage mechanical desliming versus 2-stage mechanical followed by slime flotation desliming at two levels of flocculant. Highest I.R. recovery, 81% was achieved with 3-stage mechanical desliming. Comparable IR recovery was also achieved with 2-stage mechanical plus slime flotation with lower flocculant (10 g/t) concentrations. The lowest IR content in the flotation feed was also achieved with 3-stage mechanical desliming.

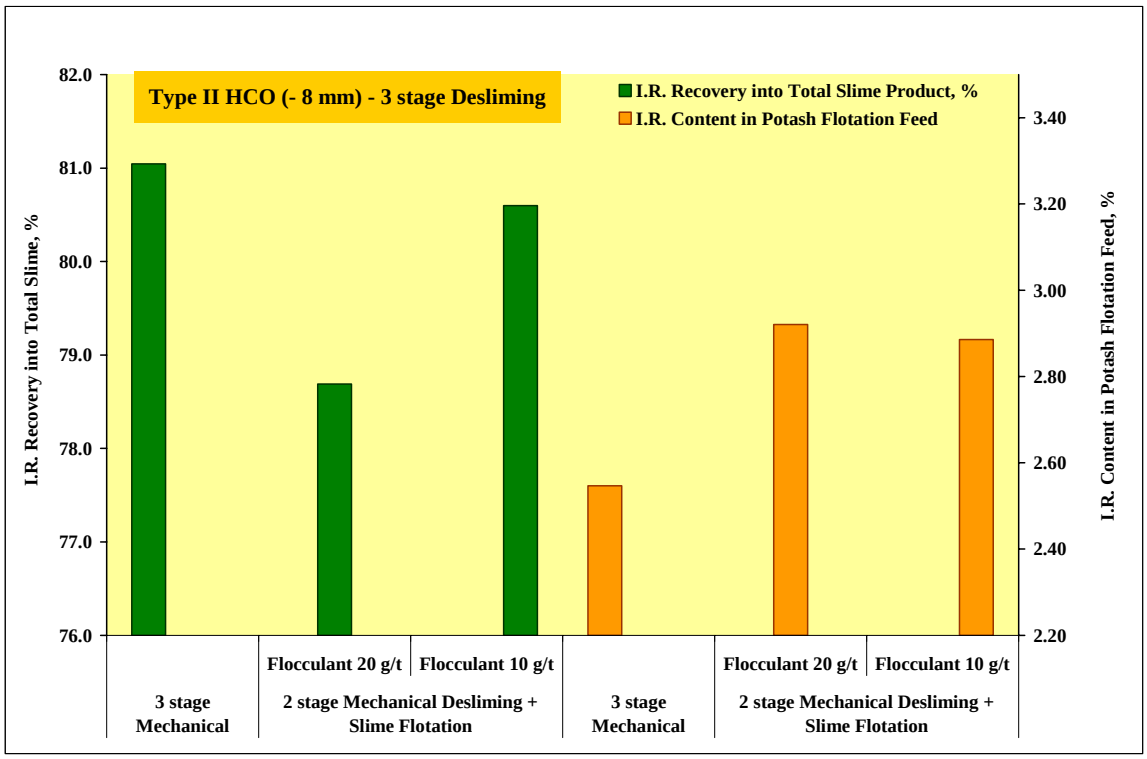


Figure-1. Comparison of total I.R. recovery into slime and I.R. content of flotation feed.

Slime flotation also slightly increased the K2O loses to slimes as shown in Figure-2. However, the slime flotation concentrate can be further cleaned by cleaner flotation where KCl entrained in the slime product can be recovered in the cleaner tailings.

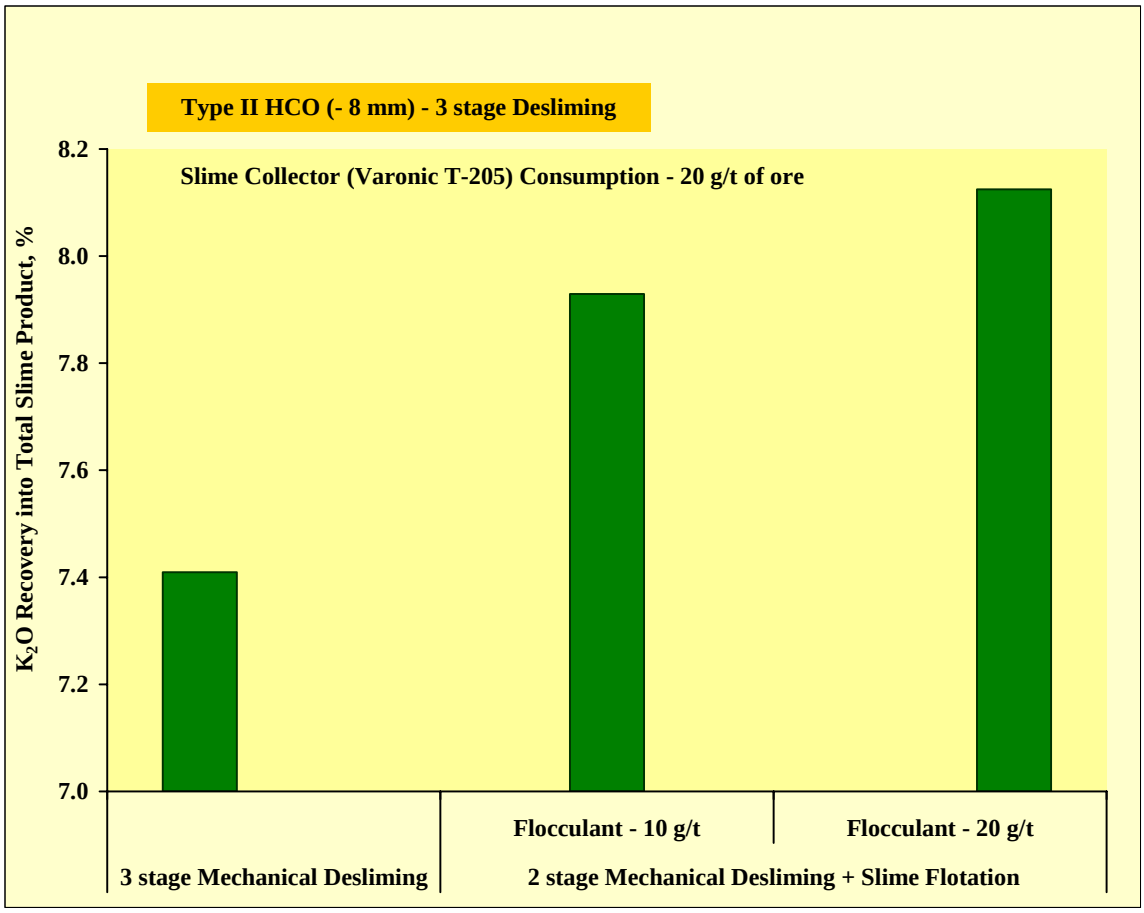
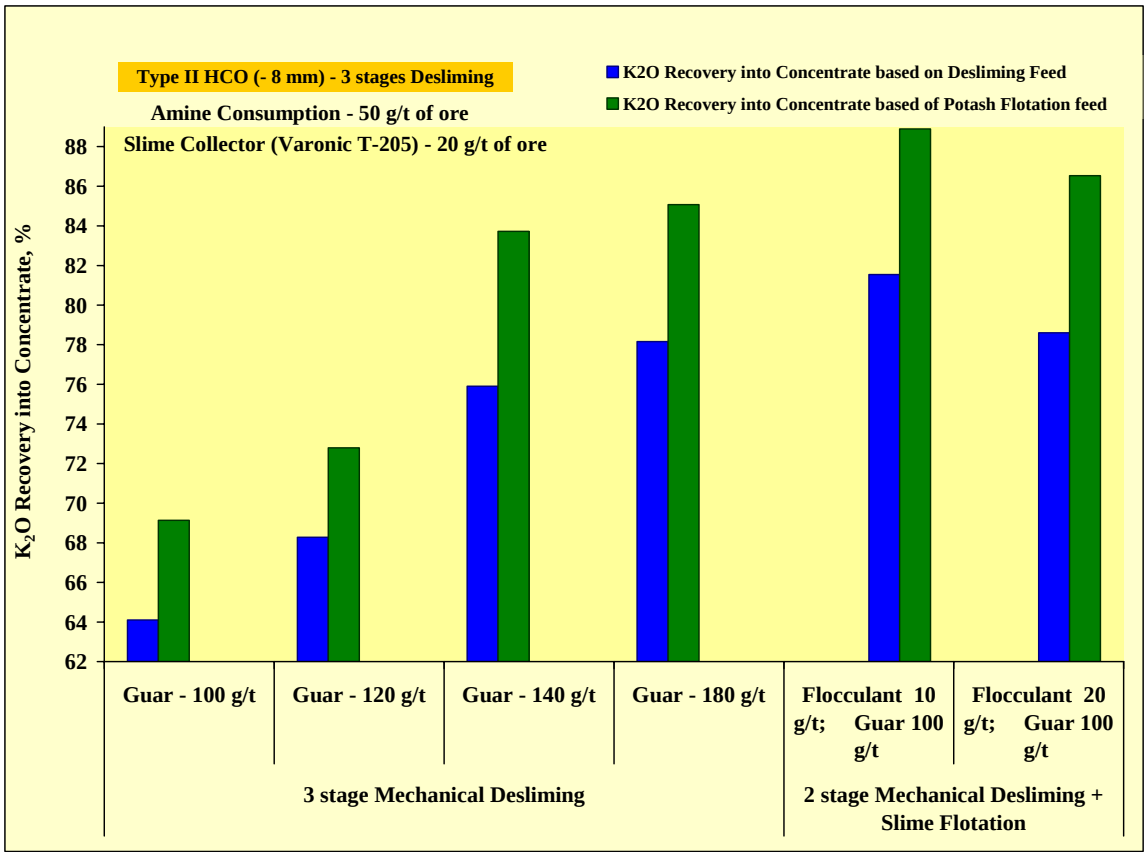


Figure-2. Potash loses into slime product.

Comparison of potash recovery into the flotation concentrate at constant amine concentration (50 g/t) is shown in Figure-3. At 100 g/t guar consumption, potash recovery is 20% higher with slime flotation desliming as compared to mechanical desliming only. It should be pointed out that even though the I.R. content of the 3-stage mechanical desliming tailings (potash flotation feed) is lower than that of the combined desliming mode, i.e., 2.5% versus 2.9% as shown in Figure-1, overall potash recoveries are much higher at the same level of guar depressant. This observation suggests that with the use of the slime flotation process surface-active fine particles susceptible to flotation, such as clay minerals as opposed to rather inert slimes (anhydrite) are preferentially removed.

It is also evident that in order to be able to achieve comparable potash recoveries with only mechanical desliming, guar consumption should be doubled and collector (amine) consumptions should also be increased.



SUMMARY

Very high clay potash ores, which heretofore could not be processed with the existing technologies, can be economically treated with combined mechanical and flotation desliming followed by potash flotation. At the same level of slime depressant and amine collector consumptions, potash recovery has increased by 20% with two stage mechanical desliming followed by slime flotation. Reversing the order of slime flotation reagents, i.e., flocculant and slime collector, reagent consumptions decreased drastically, at the same time decreasing KCl loses to the slimes. Addition of inorganic dispersants, such as aluminum sulfate to the first stage coarse desliming also improves desliming efficiency as reported in the previous progress reports.

FUTURE WORK

In light of these observations, screening tests conducted with the commercially available slime flotation collectors, oxyethylated fatty acids and fatty amines, as reported for low and medium clay ores in the previous reports, have been reexamined. Preliminary observations confirm the above conclusions that by reversing the order of flocculant and slime collector addition into the pulp, the reagent consumptions and KCl loses to slimes can be reduced drastically. These results will be presented in the final report.

Appendix 3: Column Flotation of Relative Coarse and Fine Dolomitic Phosphate Pebbles (WV007)

TECHNICAL PROGRESS REPORT

Contract Title and Number:	Period of Performance:
Crosscutting Technology Development at the Center for Advanced Separation Technologies (DE-FC26-02NT41607)	Starting Date: 10/1/2004 Ending Date: 10/31/2007

Sub-Recipient Project Title:	Report Information:
Column Flotation of Relatively Coarse and Fine Dolomite Phosphate Pebbles	Type: Semi-Annual Number: 7 Period: 3/31/06-10/31/06
Principal Investigators:	Date: 09/29/06
Peng	Code: WV007-R07
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No subcontracts issued.	Phone: Fax: E-Mail:

ABSTRACT

In this reporting period we focused on the studies of pH effect on the dolomite flotation and interaction of dissolved spices effect on the depletion of collector, in the real dolomitic phosphate ore flotation, and compared with the published theoretical pure dolomite and francolite mineral flotation system. The details of the findings are reported.

INTRODUCTION

Background

To removal of guange materials from phosphate rock containing carbonaceous gangues such as calcite, magnesite, and dolomite is complicated due to the similarities in the chemical composition and semi-soluable nature of the constituent mineral. In many flotation schemes, the poor flotation selectivity is obtained. The published works have shown that surface conversion and dissolved mineral speices-surfactant interactions are major reasons for the poor selectivity in the flotation separation of various salt type minerals. Thus to understand the mechanisms of dolomite flotation in the reverse flotation system, including the depletion of collector due to the dissolved minerals in the sparingly dissolved minerals such as dolomitic phosphate ore, and pH effect on the dolomite flotation are very important for successfully removal of dolomite from the high content of dolomite in the dolomitic

phosphate ore. There are published data and theory for dolomite removal from pure dolomite mineral and francolite mineral flotation system, using oleates collector. However there is no published data and the theory for dolomite removal from natural dolomitic phosphate ore flotation system.

Objective and Approach

The objectives are to study: 1) the pH effect on the dolomite removal from high content of dolomite in the nature dolomitic phosphate ore; and 2) the effect of dissolved Ca^{2+} and Mg^{2+} ions on the depletion of oleate collector in the reverse flotation system, using FAS-40A as oleate collector.

PROJECT TASKS

Task 1: To collect the Florida dolomitic phosphate ore samples for this researcg orihect. Two batches of samples A and B have almost used-up for the fine and coarse size particle dolomitic phosphate flotation. Te third batch of the sample C has been received from Mosaic, FL. Sample C is in the process of material characterization.

Task 2: Batch flotation of relatively coarse particle has been tested using Sample B to determine the basic reagent requirements and flotation conditions for column flotation. Flotation column has been set-up, but it is in the process of modifying column and operation conditions for fine and relative coarse particle flotation.

Task 3: More details of understanding of pH effect on depressant of phosphate particles, slime effect on the dolomite-phosphate separation performance, particle size effect on the dolomite-phosphate separation performance, the effect of dissolved Ca^{2+} and Mg^{2+} ions from natural dolomitic phosphate ore on the oleate collector, are studied. The some findings are reported in the progress report.

Task 4: The relative coarse particle column flotation will be conducted based our previous experience on the fine particle column flotation, and by use of the design of experiment to determine the best flotation conditions.

SUMMARY

The flotation behaviors of dolomite mineral and francolite minerals and appatite minerals at different oleate concentrations and pH have been studies for years (Moudgil and Somasandaran, 1985; Xiao and Somasundaran, 1989; Moudgil and Ince, 1991). The result of dolomite floated as a function of pH is exhibited in Fig. 1. Figure 1 shows that the flotation of francolite single mineral can be achieved at pH 9.0 and above, and dolomite mineral flotation can be achieved at pH 5.0 and below. Those investigators also reported there was no selective separation when the mixture or dolomite and francolite single minerals samples are used. The explanation was that,

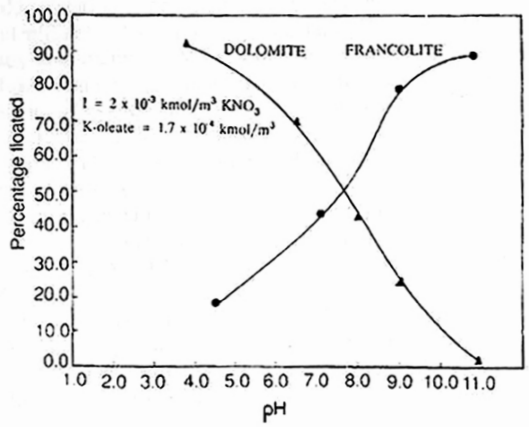

Figure 1 Flotation of francolite and dolomite minerals as a function of pH at 1.7 x 10^{-4} kmol/m^3 K-oleaic acid.

the loss of the selectivity of separation of dolomite from francolite or apatite minerals could be attributed to the alteration of the surface properties of both minerals by the dissolved mineral species. So far there is no realistic reports of the flotation behaviors for the natural dolomitic francolite ore flotation due to the extreme complexity of the components involved in the ore flotation system. To understand the interaction of dissolved species and surfactant, and pH effect on the dolomitic-phosphate ore flotation is very important to control and achieve the selective dolomite flotation and maximize the recovery of phosphate from dolomitic phosphate ore.

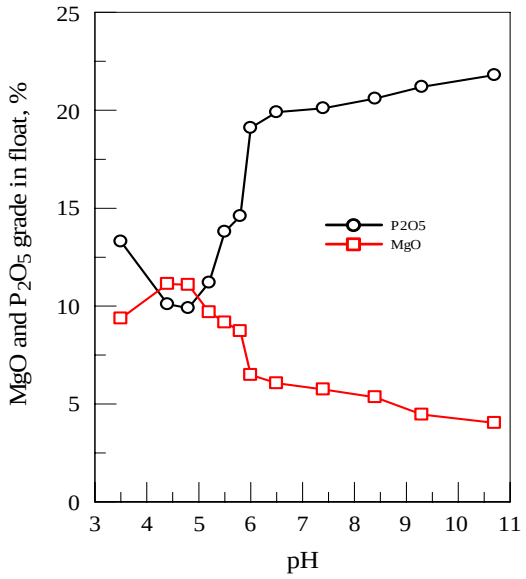

Fig. 2 MgO and P_2O_5 grade in the float of the dolomitic phospahte flotation as a function of pH.

In this study, Florida high dolomitic phosphate ore with 3.35% MgO content was used to evaluate the effects of dissolved species interacted with surfactants and pH on the flotation performance of separating dolomite from dolomitic phosphate ore. A selective fatty acid soap, FAS-40A, was used as dolomite collector, sodium hydroxide and phosphoric acid were used as pH modifiers. At pH grater than 6, it is considered as phosphate flotation rather than dolomite flotation. The collector dosage was set at 2.5 kg/t of feed for each flotation test. In order to raise the pH for high pH value, only sodium hydroxide was used, and there was no depressant (phosphoric acid) applied to inhibit the phosphate flotation. In Fig 2 the MgO and P_2O_5 grades in the float of the dolomitic phosphate ore flotation as a function of pH is presented. Figure 2 shows that, to some extent, MgO-pH grade curve mirrors P_2O_5–pH grades curve. This suggested that the higher MgO content removal corresponding lower P_2O_5 grade loss, or vise versus in the dolomite float. When pH is lower than 4.5, MgO grade increases and P_2O_5 decreases with the increase of pH. When the pH falls between pHs 4.5 and 6, there is a sharp increase in P_2O_5 grade and a sharp decrease in MgO grade. When pH is greater than 6, only gradually changes in both MgO and P_2O_5 grades are shown. Figure 2 clearly demonstrates that dolomite flotation of dolomitic phosphate ore is not much of the resemblance to the results shown in Fig 1. At pH lower than 4.5, the MgO grade-pH curve goes downward, rather than upward as shown for the dolomite and francolite minerals flotation as shown in Fig. 1. On the contrarily, the P_2O_5 grade-pH curve goes upward for the dolomitic phosphate ore flotation, rather than downward for the dolomite and fancolite mineral flotation shown in Fig. 1. The distinctive differences between the flotation behaviors in the pure dolomite and phosphate single mineral flotation system, and the realistic flotation behaviors of dolomitic phosphate ore flotation system, are obvious.

Figure 3 presents the MgO and P_2O_5 recoveries in the dolomite float, and Separation Index (SI) for dolomitic phosphate ore flotation process at various pHs for dolomitic phosphate ore flotation sytem. The results also do not show the recoveries trends of MgO and P_2O_5 as reported by Xiao and other investigators for the pure dolomite and phosphate single

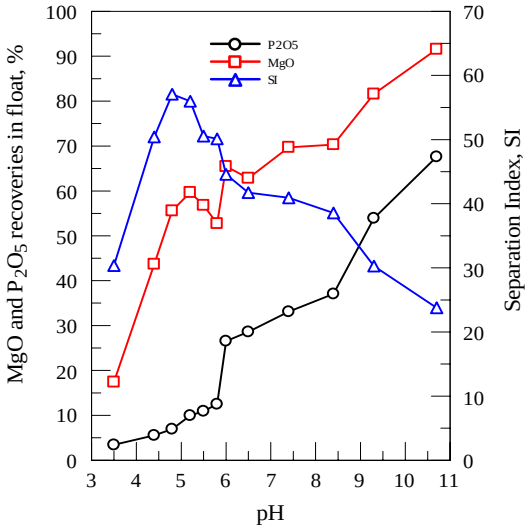

Figure 3 MgO and P_2O_5 Recoveries in the float of dolomitic phosphate ore flotation and Selective Index of dolomite as a function of pH.

minerals flotation system. The flotation recoveries of both dolomite and phosphate in the float increase with the increase of pH, and the MgO recovery is higher than P_2O_5 recovery. At pH 3.5, both dolomite and phosphate was depressed and their recoveries are quite low. From pH 3.5 to 5.4, the MgO recovery increases very sharply and reaches it peak around pH 5.4, while there is only slow increase in P_2O_5 recovery. When pH is greater than 5.4 the MgO recovery decrease. As pH above 6, a sharp increase in both MgO and P_2O_5 recoveries is observed. This is because there was no phosphoric acid being used in this flotation tests in order to obtain neutral pH and higher pH after pH 6. In this study, the phosphoric acid is considered as both pH modifier and phosphate depressant in dolomite flotation. Without addition of the depressant, much more phosphate was floated with very poor selectivity, and the dolomite also float with phosphate. This tendency continues from neutral pH through out the range of alkaline pH. The large difference between MgO and P_2O_5 recoveries in the float and sink shows a good selectivity for the dolomite separation. It can be seen that, the large difference occurs in the range of pH 4.5 to 5.8. By considering the grade and recovery of phosphate and dolomite removal, the Separation Selectivity Index curve in Fig. 3 shows that best separation of dolomite from dolomitic phosphate ore can be achieved at about pH 5.0.

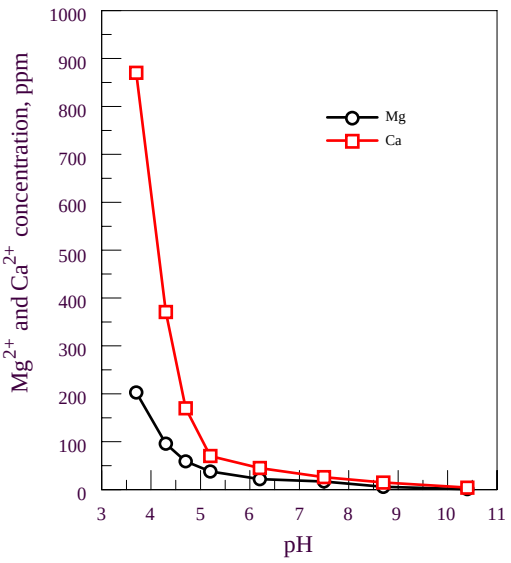

Figure 4 Ca^{2+} and Mg^{2+} concentration in the dolomitic phosphate ore flotation system using FAS-40A (2 kg/t) collector as a function of pH.

.The interactions between dissolved mineral species and surfactants leading to precipitation play a crucial role in many industrial separation processes such as in the flotation of sparingly soluble minerals, particularly, phosphate rock contained carbonaceous gangue minerals including calcite and dolomite minerals. The separation process of dolomite-dolomitic phosphate ore is complicated by the similarities in the chemical compositions and the semi-soluble properties of the constituent minerals (Hanna and Somasundaran, 1976). Poor selectivity in the separation of dolomite often reported in many flotation processes. The surface conversion and dissolved mineral species-surfactant interactions can be the contributed factors causing the poor selectivity in the flotation for various salt-type mineral systems.

It is thus essential to make clear the mechanisms involved in the interactions of surfactant with dissolved mineral species from salt-type minerals. Therefore, in this study, Ca^{2+} and Mg^{2+} concentrations in the dolomitic phosphate ore flotation system using FAS-40A at different pH are determined, and the results are plotted in Fig. 4. As expected both Ca^{2+} and Mg^{2+} concentrations increase with the decrease of pH in the ore flotation system. There is a sudden increase the dissolution of both ions at pH 5. The concentration of Ca^{2+} ion is much higher than that of Mg^{2+} ion because Ca^{2+} ion may be dissolved from dolomite, calcite and phosphate ores, and Mg^{2+} ion may be dissolved from dolomite only. Xiao and Somasundaran conducted a series of investigations on the surface and bulk precipitation of oleates in the dolominte and francolite single minerals flotation system. They found that, the dissolved calcium and magnesium ions reacted with oleates to form Ca-oleates and Mg-oleate, which lead to depletion of the collector used in the flotation system. Those authors concluded that the interactions between dissolved mineral species and oleates leading to the formation of surface and bulk precipitates might attribute to the loss of selectivity in oleate flotation of dolomite and francolite single minerals system.

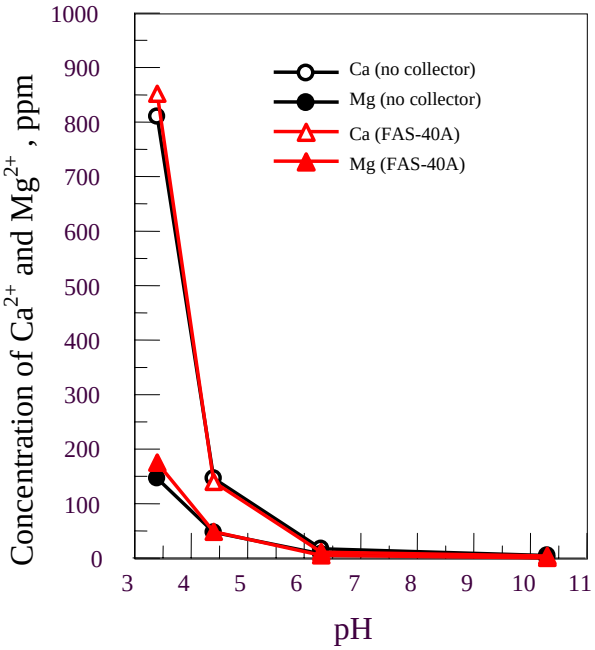

Figure 5 Effect of FAS-40A collector on the dissolution of Ca^{2+} and Mg^{2+} concentrations in the dolomitic phosphate ore flotation system.

Figure 5 presents the Ca^{2+} and Mg^{2+} concentrations at different pH in the dolomitic phosphate ore flotation system, using fatty acid soap, FAS-40 collector. The results show that, there is not much difference in Ca^{2+} and Mg^{2+} concentrations changes in the solution in the presence and absence of fatty acid soap, FAS-40A collector. Apparently there is not much of precipitation occurred by the interaction of FAS-40A surfactant with dissolved Ca^{2+} and Mg^{2+} species in the dolomitic phosphate ore flotation system. According to our findings, the flotation behaviors of dolomite in the nature dolomitic phosphate ore separation system is quite different from what have been concluded and predicted from the fundamental studies of the flotation behaviors of pure dolomite single mineral in the francolite or apatite single mineral flotation system. This includes the interaction of dissolved Ca^{2+} and Mg^{2+} ions with surfactant, the precipitation of Ca ion and Mg iron with oleate collector, and dolomite and phosphate recoveries in the float as a function of pH.

FUTURE WORK

The work will continue on the characterization of new dolomitic phosphate pebble sample C, and prepare for relatively coarse particle flotation. The slime effect and particle

size effect on the dolomite-phosphate separation performance will be continued to measure. The sample C will be further prepared for relative coarse particle batch flotation to determine the reagent conditions. The flotation column modification and testing for relative coarse particle flotation will also continued.

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PUBLICATIONS/PRESENTATIONS

Technical papers entitled “Effect of particle size on dolomitic phosphate flotation”, and “Fine dolomitic phosphate pebble in modified packed column flotation”, are in preparation.

Appendix 4: Beneficiation of Mixed Potash Ores From New Mexico (NM004)

TECHNICAL PROGRESS REPORT

Contract Title and Number:	Period of Performance:
Crosscutting Technology Development at the Center for Advanced Separation Technologies (DE-FC26-02NT41607)	Starting Date: 6/1/2004 Ending Date: 10/31/2006

Sub-Recipient Project Title:	Report Information:
Beneficiation of Mixed Potash Ores from New Mexico	Type: Semi-Annual Number: 3 Period: 4/01/06-9/31/06
Principal Investigators:	Date: 09/06/06
I. Gundiler, L. Brandvold, T. Pietras, S. Titkov	Code: NM004-R03
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ABSTRACT

Processing mixed potash ores requires recovering K-Mg double sulfate salts from sylvite tailings and selective separation of these minerals from mixed concentrates. However, very little information is available on the flotation characteristics of mixed salts. Representative ore and concentrate samples were collected from operating plants and analyzed. Bench and micro flotation tests and fundamental studies, such as NMR and zeta potential measurements, were initiated. So far, flotation was only achieved with fatty acid collectors.

INTRODUCTION

Background

Potash is the common term that denotes the element potassium in a water-soluble form in a variety of chemical combinations. The potassium content in potash ores and fertilizer products is reported as $\%K_2O$ as a means to compare different potash minerals.

The most abundant potash ore, sylvinite, is a mechanical mixture of sylvite (KCl) and halite (NaCl), including minor amounts of clays, silica, anhydrite ($CaSO_4$), and potassium

complexes as carnallite, polyhalite, kainite, langbeinite and leonite. The chemical composition of principal potash minerals is given in Table 1. Sylvinite and langbeinite are the only major ore minerals mined in New Mexico. Langbeinite is mined and processed only in New Mexico.

Table 1. Common potash minerals.

Mineral	Formula	Specific gravity	% K_2O
Sylvite	KCl	1.99	63.17
Carnallite	$KCl.MgCl_2.6H_2O$	1.60	16.95
Kainite	$KCl.MgSO_4.3H_2O$	2.13	18.92
Langbeinite	$K_2SO_4.2MgSO_4$	2.83	22.70
Leonite	$K_2SO_4.MgSO_4.4H_2O$	2.25	25.69
Schoenite	$K_2SO_4.MgSO_4.6H_2O$	2.15	23.39
Polyhalite	$K_2SO_4.MgSO_4.2CaSO_4.2H_2O$	2.78	15.62

Low chloride content and lower solubility of the potassium sulfate products make them desirable for certain crops, such as tobacco, potato, and citrus crops, and soil conditions. Langbeinite is less soluble than halite; high-grade ores are simply leached with water to produce 22% K_2O concentrates. The specific gravity and solubility of polyhalite and kieserite ($MgSO_4 \cdot H_2O$) are both similar to langbeinite. Hence, they remain with the concentrate and lower the product grade. The water leaching method of producing a marketable grade langbeinite, however, requires high water consumption that has a significant impact on the region.

Langbeinite in mixed sylvite - langbeinite ores could range as high as 15% by weight; langbeinite and other double (K-Mg) sulfate minerals cannot be recovered at present and they are lost to the sylvite tailings. There are also large reserves of langbeinite ore that are not exploited due to high concentrations of kieserite contamination. If kieserite can be separated from langbeinite, it can be marketed as soil amendment additive. An efficient method to separate fine halite and kieserite from langbeinite does not exist.

Early literature suggests that langbeinite flotation has been practiced briefly at the Stebnik mine in Ukraine (CA 67, 13345z, 1967), and kieserite flotation was utilized to separate it from sylvite and halite from Hartsalz ores in Germany in 1960s. It appears that kieserite flotation is sensitive to the brine composition, pH, and collector concentration. Singewald (Ger. Patent, 1,159,871, 1963) claimed separation of kieserite and langbeinite with oleylamine oleate as a collector at pH 4-7 in water or very dilute brine. Schubert (Ger. Pat. 1,224,676, 1966) claimed flotation of kieserite in saturated sylvite brine (KCl-NaCl) containing $MgCl_2$ and $MgSO_4$ with fatty acid sulfonates and oleylmethyltauride.

Recently Hancer and Miller (2000) investigated the flotation behavior of K, Mg double salts, kainite, schoenite, and carnallite. They attributed the peculiarities in the flotation behavior of these minerals to the differences in the interfacial water structures.

Objectives and Approach

The primary objectives of this work can be summarized as i) recovery of langbeinite and kieserite from sylvite tailings, ii) flotation separation of langbeinite and kieserite from mixed concentrates, and iii) flotation separation of halite from langbeinite ores to produce high-grade langbeinite concentrates. Secondary objectives are to investigate the effects of magnesium ion concentration, brine temperature, and amine composition on sylvite flotation to develop a better understanding of fundamental aspects of soluble salt flotation.

PROJECT TASKS

Task 1 - Materials and Methods

Several drums of sylvite ores and plant brines were collected from potash processing plants in Carlsbad, NM and brought to our laboratories. In addition, several hundred pounds of mixed sylvite-langbeinite, high-grade langbeinite, langbeinite ore with high-kieserite content, and coarse langbeinite gravity concentrates were also collected. A large sample of kieserite concentrate from Germany was also procured and washed with caustic solutions to remove the fatty acid residues used to generate charge for electrostatic separation of kieserite from sylvite.

Analyses of all the above mentioned ore samples and concentrates were conducted and mineralogical compositions were determined using the Fuchsman method, based on the Na, K, Ca, Mg, Cl, and sulfate ion concentrations and water of hydration at 110, 330, and 440 C. Flotation concentrates and tailings were analyzed similarly. Samples were prepared for micro-flotation testing, zeta potential measurements, and NMR studies.

Task 2 – Experimental Results and Discussions

Micro-Flotation Tests

Samples of relatively pure kieserite and langbeinite were prepared from concentrates. Flotation of these minerals either individually, or from mixtures of sylvite flotation tailings were tested using a number of anionic and cationic collectors in dilute NaCl as well as NaCl-KCl brines. The anionic collectors tested include short and long chain fatty acids, sulfates, and sulfonates. Short and long chain amines were also tested for kieserite flotation. Initial experiments conducted in a 1-L flotation cell did not produce reproducible results due to difficulty in adjusting agitation speed, and low pulp density used in screening tests. Subsequently, a 150 ml column flotation cell, and a 400 ml mechanical flotation cell were used. Complete results of these tests are not yet available; initial observations suggest that fatty acids, such as tall oil, float both langbeinite and kieserite. Selective separation of these minerals has not yet been achieved and would require further studies. Sulfates and sulfonates either showed no collector ability, or very slow kinetics and excessive foaming.

NMR Studies and Zeta Potential Measurements

In order to develop a better understanding of flotation behavior of langbeinite and kieserite fundamental studies were initiated. Kieserite and langbeinite concentrates were

washed with caustic solutions to remove residual reagents, rinsed with water and dried. The samples were then ground and screened. Minus 0.3 mm (48 mesh) plus 0.1 mm (150 mesh) fraction is being used for micro flotation tests using 10 gr. samples. The minus 37 μm fraction is being used in zeta potential measurements in dilute brine, as function of pH. It is believed that these studies will help identify the conditions and reagents for separation of these minerals.

Nuclear Magnetic Resonance (NMR) studies were initiated to study the interfacial water structure of these minerals for better understanding of potash flotation. NMR spectroscopy is a powerful tool to investigate the effect of foreign ions on the interfacial water structure. By measuring the ^1H NMR spin-lattice relaxation time (T_1) of protons in water, conclusions about the mobility of water on the mineral surface can be drawn. Water molecule mobility near electrolyte ions is dependent on the charge-to-radius ratio of the ion. At ambient temperature, highly polarizing (structure-making) ions such as Li^+ and Mg^{2+} have a positive enthalpy of aquation. The rotation of the water molecule is slowed down in their presence. Ions with a lower charge density (structure-breaking) such as K^+ or Cl^- are characterized by a negative enthalpy of aquation, and an increased mobility of nearby water molecules. The ^1H NMR spin-lattice relaxation time of water is directly related to its mobility. Furthermore, the T_1 of protons in water depends on whether the surface is water-wet or oil-wet. Comparing ^1H NMR spin-lattice relaxation times of pure water and after adding structure-making or structure-breaking ions, and finally, a combination of the two, will help to clarify the concerted effect of these ions on the floatability of KCl. Temperature dependent studies will further contribute towards the understanding of soluble salt flotation.

Brine solutions were prepared by adding an excess of NaCl, KCl, 1:1 KCl and $MgCl_2$ (KCl-$MgCl_2$) or 1:2 KCl and NaCl (KCl-2NaCl) to water. The solutions were allowed to stand at room temperature for several days to come to equilibrium. The brines were added to NMR tubes and T_1 values were measured. Then reagent grade NaCl and KCl were added to the appropriate brines and allowed to settle through the solution to the bottom of the tubes and T_1 values were again measured. Dodecylamine (DDA) neutralized to pH 5 with HCl, and dodecyl sulfate (DDS) solutions in de-ionized water were added to respective brines to yield 10^{-6} M solutions. Actual concentrations could be less because of reduced solubility in brines.

For the brines containing solids, sample positioning was critical. Great care was taken that only the solid interspersed with brine was enclosed by the NMR pick-up coil. When the solid-liquid interface (the solids settle at the bottom of the NMR tube) was moved into the region of the NMR pick-up coil, the ^1H NMR signal was composed of two components: a narrow one, representing the brine above the interface, and a broad one, representing the brine in the inter-particle space of the solid. When moving the sample up so that the solid-liquid interface was no longer enclosed by the NMR pick-up coil, the line shape revealed only one component, namely the broad one, originating from the brine in the inter-particle space. T_1s were measured in this sample position.

NMR data were recorded on a Jeol 300 MHz NMR spectrometer. The temperature was controlled and maintained at 298 K. Spin lattice relaxation time constants, T_1, were determined using the inversion recovery technique with a ^1H 90° pulse width of 13 μs. About

20 different inter-pulse delays were included to precisely define the magnetization recovery curve.

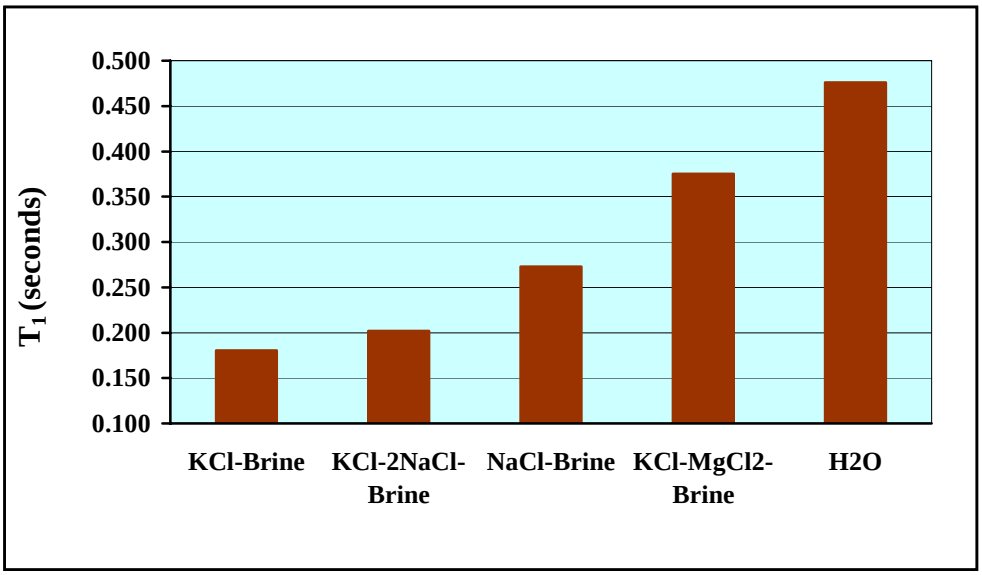

Figure-1. T_1 values for water and 4 different brines.

Values for ^{1}H NMR T_1 for water and the different brines are presented in Figure 1. In free water, ^{1}H relaxation is hindered through hydrogen bonding. In order for relaxation to occur, fluctuations of magnetic fields on the order of the Larmor frequency must be present. These fluctuations are often induced by molecular motion. In pure water, this motion is hindered through hydrogen bonding. In brine, the presence of ions 'interrupts' this type of bonding, and the water molecules experience greater mobility leading to shorter T_1s, as observed.

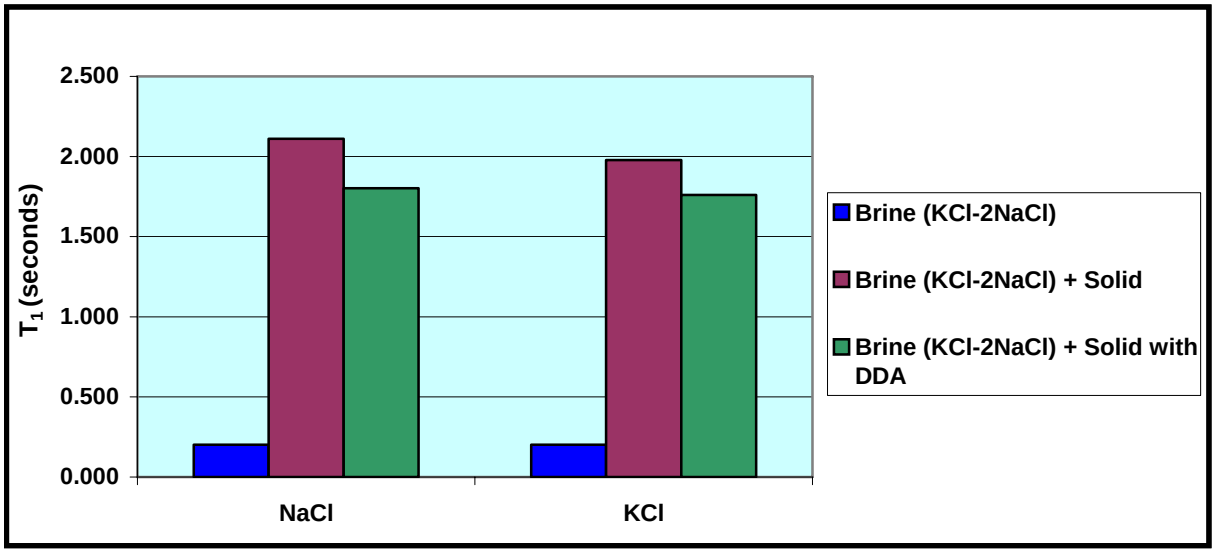

Figure-2. Comparison of T_1 values for KCl-2NaCl brine with and without KCl or NaCl and with and without DDA collector.

Figure-3 further shows the effect of DDS or DDA collector on the KCl brine system. Both collectors reduce T_1 to a similar degree.

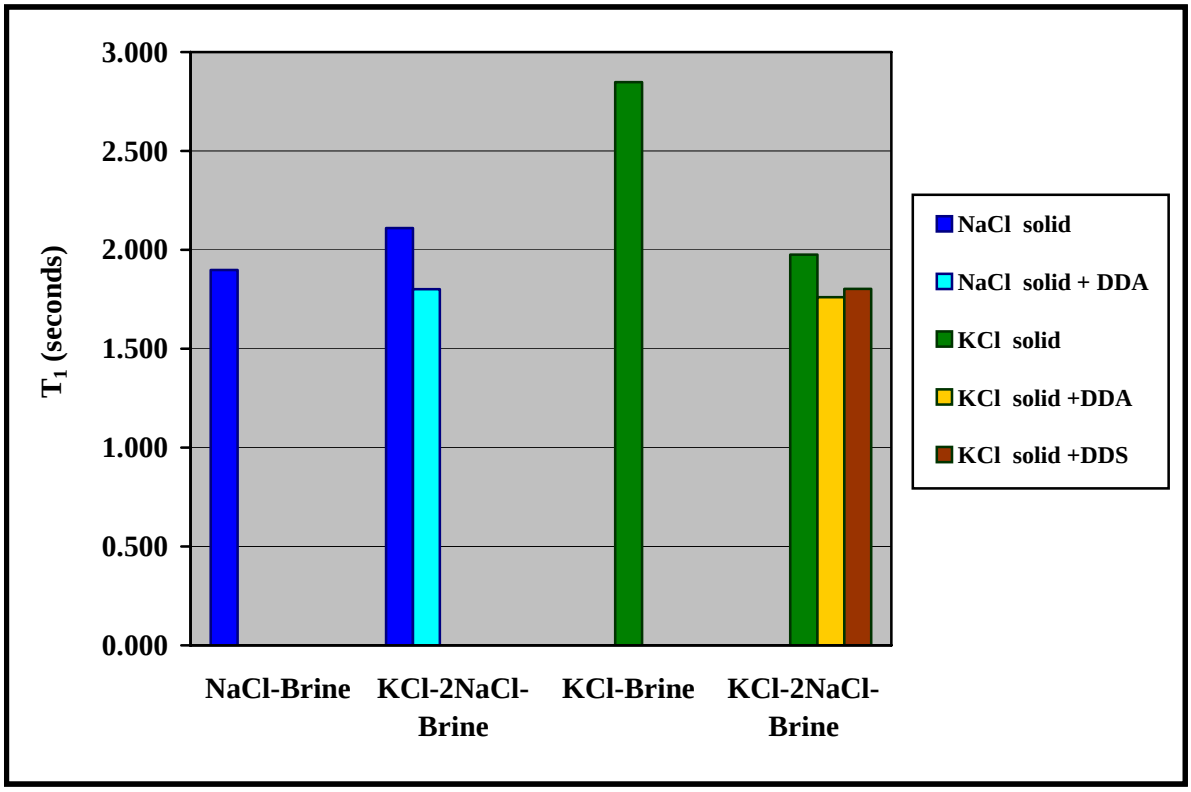

Figure-3. Comparison of T_1 values for different brines with solids NaCl or KCl with and without collectors, DDA and DDS.

SUMMARY

Sylvite-langbeinite mixed ore, high-grade langbeinite ore, high-kieserite langbeinite ore samples, langbeinite gravity concentrates and kieserite concentrates were collected, analyzed and mineralogical compositions were determined. Samples were prepared and a series of flotation tests were carried out with long and short chain fatty acids, fatty amines, sulfates, and sulfonates. So far, flotation of sulfate minerals was achieved only with fatty acid collectors. NMR studies to better understand soluble salt flotation were initiated along with zeta potential measurements in dilute brines as a function of pH.

FUTURE WORK

Micro-flotation tests using relatively pure mineral samples are currently being carried out using commercially available reagents. An attempt is being made to synthesize the reagents suggested in the literature for selective separation of langbeinite and kieserite, or used in the past kieserite or langbeinite flotation operations. Fundamental studies will also be continued with Mg bearing minerals.

REFERENCES

Hancer, M. and Miller, J.D., 2000, “The Flotation Chemistry of Potassium double Salts: Schoenite, Kainite, and Carnallite”, Minerals Engineering, Vol. 13, pp. 1483-1493.

Appendix 5: Development of a New Reagent Schedule for Flotation of Dolomite from Phosphate Ores (NV002)

TECHNICAL PROGRESS REPORT

Contract Title and Number
Establishment of the Center for Advanced Separation Technologies (DE-FC26-01NT41091)

Period of Performance
Starting Date: 6-1-2004
Ending Date: 10-31-2007

Sub-Recipient Project Title:
Development of New Reagents for Flotation of Dolomite from Phosphate Ores

Report Information:
Type: Semi-Annual
Number: 4
Period: 4-1-06 to 9-30-06
Date: 8-24-06
Code: NV002-R04

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ABSTRACT

Two types of reagents were tested for selective phosphate rock flotation, betaine analogs and sarcosine analogs utilizing microflotation experiments. Decyl betaine, tetradecyl betaine, and a variation of decyl betaine were tested as collectors but failed to show significant recovery. Sarcosine analogs, lauroyl, myristoyl and palmitoyl, were also tested as collectors and showed strong collector properties for apatite and dolomite. Experiments will be run on a natural ore with a laboratory flotation cell. Electrokinetic experiments were run to better understand mechanisms of collector adsorption.

INTRODUCTION

The United States is the largest phosphate rock producer in the world. About 30 % of the total world production in 1990 was produced by the United States (1). Florida accounts for approximately 80 % of the U.S. phosphate production (2). During the past 100 years, the Florida phosphate industry has produced high quality products having a MgO content of less than 0.5 %. Phosphate reserves and resources in Florida have the potential to continue production at a rate of about 40-55 million metric tons/year for hundreds of years (3).

Resources with relatively-low MgO (dolomite) content are being depleted, and future production is going to have to utilize those resources containing significant dolomitic carbonate. The processing of these reserves will require special beneficiation techniques to produce concentrates containing less than the practical limit of about 1 % MgO.

Over the past several years, five flotation processes have been developed to separate dolomite from phosphate or phosphate from dolomite (4). They are the TVA (Tennessee Valley Authority) phosphonic acid process, the UF (University of Florida) two-stage conditioning process, the University of Alabama process, the USBM (United States Bureau of Mines) process, and the IMC (International Minerals and Chemical Corporation) cationic process.

None of these processes has been commercialized for a variety of reasons. In order to further exploit Florida dolomitic phosphate pebbles and to improve phosphate beneficiation, the development of effective collectors for dolomite appears to be essential.

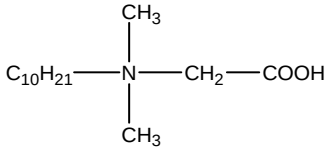
Objective and Approach

The objective of this investigation is to synthesize collectors that have specificity for magnesium and, hence, dolomite. Flotation characteristics of apatite, dolomite and phosphate rock will be determined with those collectors to establish whether physical separation of dolomite from phosphate rock can be obtained.

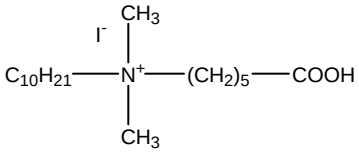
PROJECT TASKS

Flotation Collector Synthesis

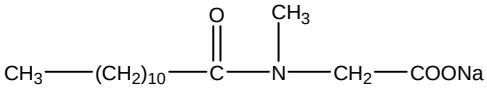
Analogs of betaine and sarcosine were designed and synthesized. Three variations of the betaine molecule were made: decyl betaine, tetradecyl betaine, and a variation of the decyl betaine (carboxypentyldimethyldecylammonium iodide). The variations in the first two betaines are in the principal alkyl carbon chain length. Decyl betaine variation contains an additional pentyl group between the nitrogen and carboxyl group.



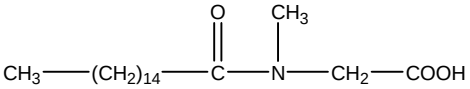
N-Decyl Betaine



N-Decyl Betaine variation



Lauroyl Sarcosine Salt



Palmitoyl Sarcosine

Lauroyl sarcosine was purchased from a vendor, while myristoyl and palmitoyl sasrcosines were synthesized in the laboratory. The sarsosines were prepared by dissolving sarcosine in methanol, neutralizing with sodium hydroxide, combining with myristoyl or palmitoyl chloride,

acidifying, and extracting with diethylether.

Flotation Experiments

Flotation experiments were conducted with the synthesized betaines and sarcosines as collectors for apatite and dolomite using a Hallimond tube. One gram of mineral, 150 x 106 µm, was added to 150 ml of solution. Conditioning was conducted for three minutes at the desired collector concentration and pH. Each sample was floated for one minute with nitrogen gas bubbled through the Hallimond tube at 0.06 SLPM. Collector concentrations and pH were varied to determine the effect of each on flotation.

Betaine Collectors

Flotation experiments with both apatite and dolomite were conducted with decyl, tetradecyl and decyl (varation) betaines. The results obtained with dolomite are presented in Figure 1. It is apparent that only modest flotation is obtained even in the presence of fairly high concentrations of collector. Similar results were obtained with apatite. In this view further experimentation with betaines was discontinued.

Sarcosine Collectors

The flotation recoveries of apatite and dolomite as a function of lauroyl sarcosine collector concentration is shown in Figure 2. Both minerals are noted to respond well with this collector, with apatite floating at somewhat lower concentrations. The upper limit of recovery (90%) of the dolomite is attributed to the quartz impurity present in the dolomite sample.

The effect of pH on the flotation recovery of apatite and dolomite with lauroyl sarcosine is shown in Figure 3. The concentration of 2 x 10^{-4} M resulted in complete flotation of apatite across the pH range tested. With dolomite, however, a narrow region of depression can be noted around pH 7. This phenomenon has been noted with other collectors and dolomite. These data indicate two mechanisms of collector adsorption on dolomite which will be studied with infrared experiments.

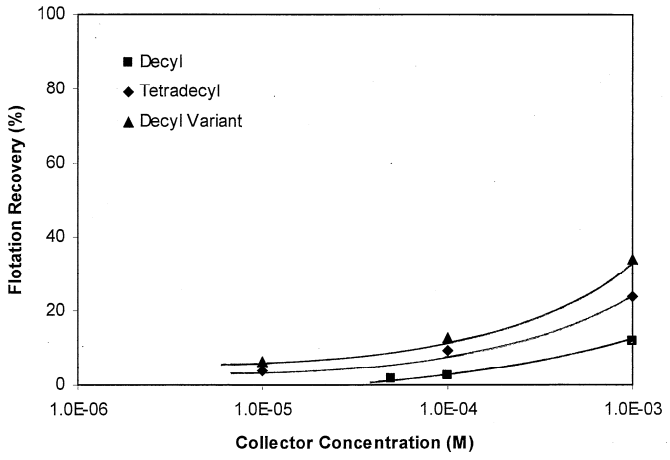


Figure 1. Flotation recovery of dolomite as a function of betaine analog concentration.

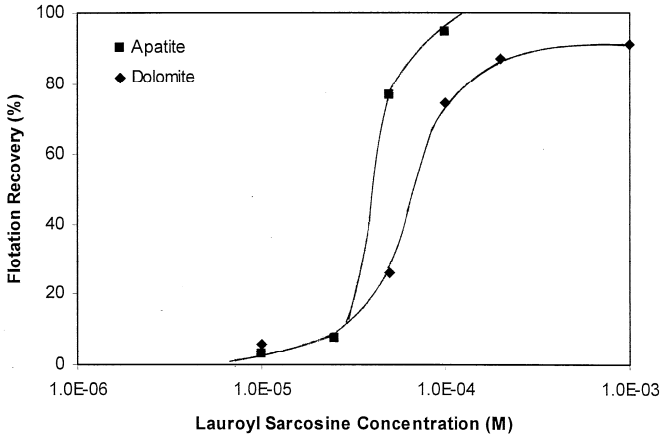


Figure 2. Flotation recovery of dolomite and apatite as a function of lauroyl sarcosine concentration at pH 9.3.

Flotation experiments have also been conducted with apatite and dolomite with myristoyl and palmitoyl sarcasines. As anticipated, flotation recovery increases at lower concentrations with increased chain length of collector. See Figure 4.

Electrokinetic Experiments

Zeta potential determinations were made with apatite and dolomite as a function of pH. These results are presented in Figure 5 and show that the pzc of these samples are pH 5.0 for apatite and pH 8.2 for dolomite.

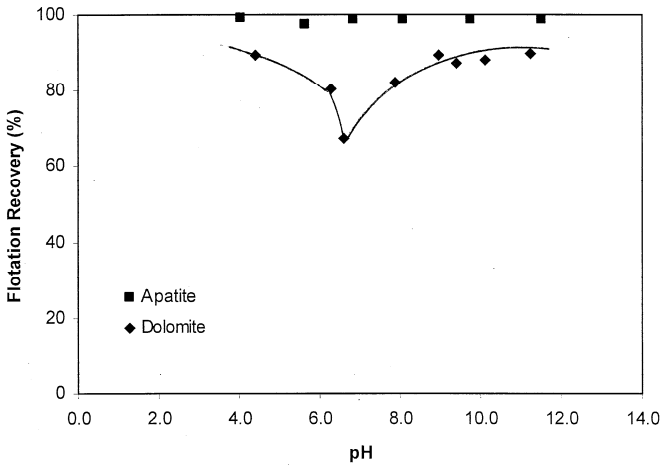


Figure 3. Flotation recovery of dolomite and apatite as a function of pH with 2 x 10^{-4} M lauroyl sarcosine concentration.

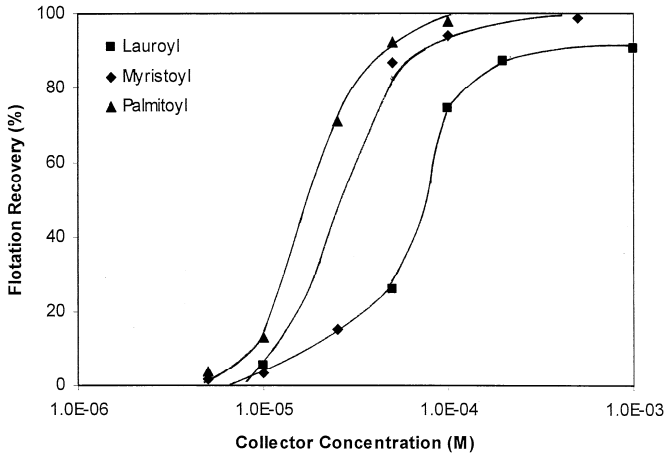


Figure 4. Flotation recovery of dolomite as a function of sarcosine analog concentration.

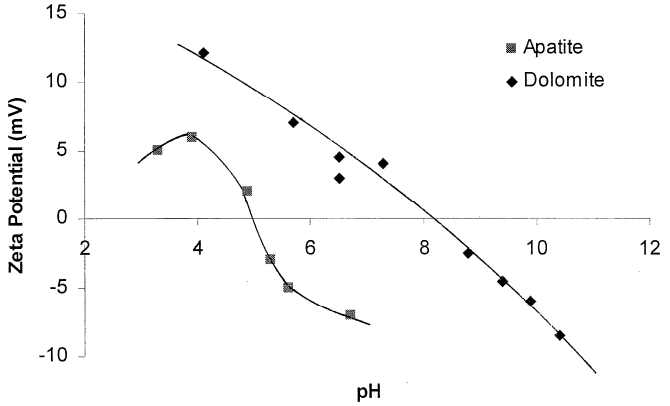


Figure 5. Zeta potential of apatite and dolomite as a function of pH in distilled water.

SUMMARY

Various analogs of betaine and sarcosine were tested as flotation collectors in a microflotation cell. None of the betaines displayed notable potential. The sarcosine analogs show strong flotation collector properties for apatite and dolomite. Electrokinetic determinations in conjunction with flotation experiments indicate that sarcosine adsorbs on dolomite by two mechanisms depending on pH. Below the pzc, sarcosine would appear to be adsorbing physically on the surface. Above the pzc, chemisorption is apparently occurring.

FUTURE WORK

Future work will involve testing the various sarcosines on a phosphate ore containing about 15 wt % dolomite. Infrared experiments will be conducted to establish mechanisms of collector adsorption to establish optimal conditions for flotation.

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1. Bartels, J. J., and Gurr, T. M. 1994. "Phosphate Rock." Industrial Minerals and Rocks. 6th Edition. D. D. Carr. Ed. Society for Mining, Metallurgy and Exploration, Littleton, CO. pp 751-764.

2. Harben, P. 1991. "Where is Florida's Phosphate Industry Going?" Industrial Minerals, No. 148. pp. 48-55.

3. Sandvik, P. O. 1979. "U. S. Phosphate-Abundant Resources Will Last for Hundreds of Years." Eng. & Min. J., 180:99-101.

4. El Shall, H. 1994. "Evaluation of Dolomite Separation Techniques. FIPR Contract No. 93-02-994, Final Report.

Appendix 6: Enhanced Flotation Performance Through Column Froth Enrichment (KY006)

TECHNICAL PROGRESS REPORT

Contract Title and Number:	Period of Performance:
Crosscutting Technology Development at the Center for Advanced Separation Technologies (DE-FC26-02NT41607)	Starting Date: 6/1/2005 Ending Date: 10/31/2006

Sub-Recipient Project Title:	Report Information:
Enhanced Flotation Performance Through Column Froth Enrichment	Type: Semi-Annual Number: 2 Period: 04/01/06-9/30/06
Principal Investigators:	Date: 10/10/06
Honaker, Tao	Code: KY006-R01
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Subcontractor Address:	Subcontractor Information:
No subcontracts issued.	Phone: Fax: E-Mail:

ABSTRACT

Several experimental programs have been performed to determine the feasibility of improving the selectivity achieved in a froth flotation column by exploiting the selective detachment mechanism. Methods evaluated include 1) the application of ultrasonic energy directly to the froth zone and 2) the injection of hydrophobic and magnetic material into the froth phase through the wash water system. The sessile drop contact angle for the magnetic plastic material was determined to be around 83^{o} whereas the contact angle for the Pittsburgh No. 8 coal sample was 65^{o}. When the plastic was added to the froth zone, over 99% of the 65 x 325 mesh plastic was recovered in the froth product. A high addition rate of plastic material displaces the coal particles and results in a significant drop in recovery. The effect on selectivity is still being evaluated. The results obtained using ultrasonics are inconclusive at this time and will be the subject of future investigations.

INTRODUCTION

Background

The froth flotation process is comprised of two separate and distinctly different zones, i.e., the collection zone and the froth zone. In the collection zone, the separation of the valuable minerals from the non-valuables is achieved based on the bubble-particle attachment process. Due to hydraulic entrainment, a portion of the non-valuable minerals is carried from the collection zone into the froth zone with the mineral-bubble aggregates. Selectivity of the process can be enhanced in the froth zone by providing drainage of the feed pulp and utilizing the selective detachment of the more weak hydrophobic particles as a result of bubble coalescence and the resulting bubble surface area reduction. The importance of the latter sub-process is the subject of recent investigations (van Deventer et al., 2004; Honaker and Ozsever, 2003; Ata et al., 2002; Ralston et al., 1999; Falutsu, 1994; Hewitt et al., 1994; Yianatos et al., 1988). On the other hand, decades of research focused on the froth flotation process have resulted in a clear understanding of the processes and sub-processes involved in the selectivity achieved in the collection zone (Yoon and Mao, 1996; Mao and Yoon, 1997).

Objective and Approach

This proposed project will exploit the selective detachment process to enhance the selectivity between particles having varying degrees of floatability. External refluxing and the addition of hydrophobic material directly into the froth zone will be investigated as described in the following sections.

PROJECT TASKS

Task 1. Fundamental Evaluation of Selective Detachment

Approximately 100 kg of 'PolyMag', which is plastic material into which magnetite has been added, was received from Eriez Manufacturing. A large block of the material was also provided from which contact angles were measured. The surface of the block was polished according to standard procedures. Sessile drop contact angles were measured and the values averaged around 83^o with a standard deviation of 3.8. The bulk sample of the magnetic plastic was crushed in a laboratory hammer mill and wet screened to obtain a 65 x 325 mesh fraction that was used in the flotation experiments.

A washability test was conducted on the as-received Pittsburgh No. 8 coal sample. Large specimens were hand selected from the 1.3 float, 1.3 x 1.6, and 1.6 x 2.0 density fractions. The samples were cut and polished for goniometer measurements. The average contact angle was 65^o for the 1.3 float fraction.

The fundamental work using methylated silica will be initiated during the second year of the project. The initial work has concentrated on the more practical aspects of the project in an effort to improve the knowledge base of the graduate student hired for the project.

Task 2. Practical Applications of Magnetic, Hydrophobic Particles

The effort in this task involves the use of a flotation column made of cylindrical Plexiglas tubing having a 5-cm inner diameter and a height of 246 cm. Feed slurry is injected at 45 cm below the overflow lip using a variable speed pump. Pulp level is maintained by utilizing a control valve to manipulate the flow rate of the tailings stream. Air bubbles are generated a static mixer of 1.9 cm inner diameter and pumping recycled tailings slurry at a pressure of 20 psi into the column. A fixed mixer was attached to a sump where feed slurry is conditioned and kept uniform with the help of another pump that allows recycle of a portion of the flow back to the sump for improved mixing. Collector is directly added to the sump while frother is injected to the recirculation stream through a peristaltic pump.

At this time, the investigation has utilized fine coal samples from two run-of-mine coal sources, i.e., Hazard No. 4 seam coal from eastern Kentucky and Pittsburgh No. 8 seam coal from southwestern Pennsylvania. Upon arrival, the samples were ground to a particle size less than 65 mesh using a laboratory jaw crusher and hammer mill.

The standard operating conditions of the column were: air flow rate at 2 cm/s, wash water 400 ml/min and 0.45 kg/ton collector rate. Samples from each process stream were collected after a time period equal to three particle retention times to ensure steady-state operating condition. For tests involving the addition of 'Polymag', each sample was processed through a high-gradient magnetic separator to remove the plastic material prior to analysis for ash content.

In the first stage of the test program, MIBC and polyglycol were used as frother at different concentrations while fuel oil No. 2 was employed as collector in the treatment of the Hazard No. 4 coal. A first set of tests were conducted to generate a baseline recovery-product ash curve by varying the volumetric feed rate without the addition of any external material. Afterward, 65 x 325 mesh magnetic plastic was mixed into the washwater at varying concentrations and injected into the froth phase using a peristaltic pump. A third set of tests involved the use of a sonifier which is a machine that transmits ultrasonic energy into a solution. The sonifier was attached to the top of the flotation column in a way that its head was immerse into the froth zone without blocking the output stream flow. The sonifier frequency rate was varied over several tests.

Flotation work was also initiated on the Pittsburgh No. 8 samples with the objective of improving sulfur rejection. A polyglycol frother was used in these tests at a concentration of 20 ppm. All separation performance results were compared with those obtained from release analysis.

Data Analysis: Column flotation results achieved on the Hazard No. 4 coal with and without the magnetic plastic material are compared in Figure 1. In all tests, over 99% of the magnetic plastic material was recovered in the froth concentrate including tests in which the solids loading exceeded froth carrying capacity limits. It is certainly not clear from comparing the results that the magnetic plastic material is improving selectivity. Furthermore, the results are inconsistent in that, at the same volumetric feed rate, the

injection of the plastic material reduces the product ash content and recovery values while under other feed rates the opposite occurs. As a result, additional tests are being performed to address repeatability and to evaluate the various component recovery performances in more detail.

A similar finding was also obtained from the application of ultrasonics as shown on Figure 2. No improvement in selectivity was observed over a wide range of product ash values. The outcomes of both the magnetic plastic and ultrasonic tests have generated a need to proceed with a more fundamental evaluation of their effects in the froth zone. Future plans include trying to secure a large sample of high quality, low ash coal that floats at 1.3 specific gravity in an effort to evaluate a more homogenously floatable coal. Also, a high density-pyrite rich material will be collected to study the impact of rejecting the pyrite from the froth using the magnetic plastic material. Separate flotation tests will be performed on the 'pure' coal and the pyrite rich material separately and as a blend.

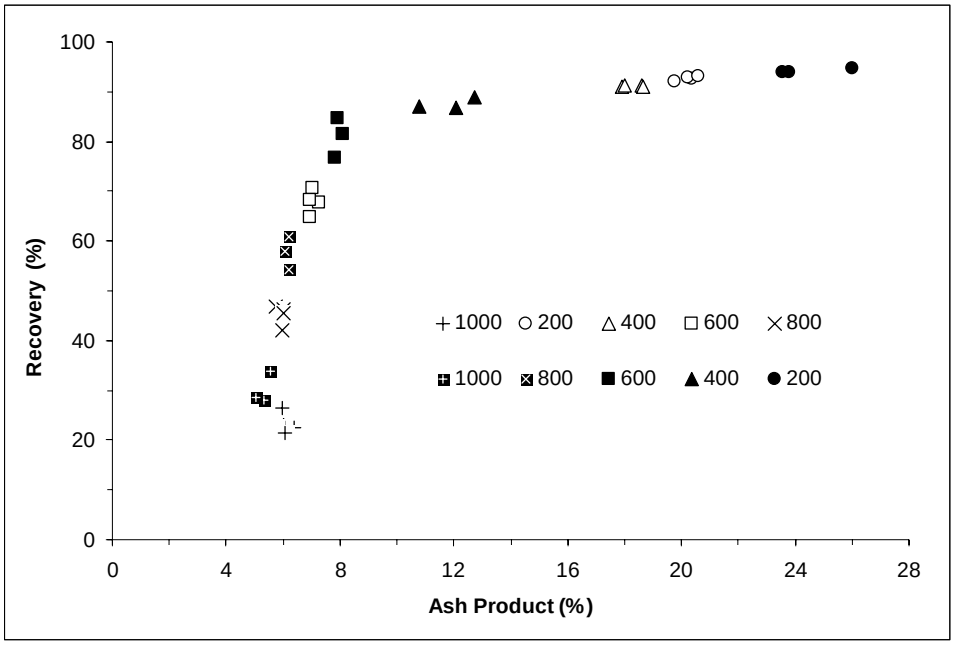

Figure 1. Column flotation data obtained without magnetic plastic material (first row) and using magnetic plastic material (second row) for different feed rate; feed solids concentration = 7.5% by weight.

Tests were initiated on Pittsburgh No. 8 coal and the initial column flotation results are compared with those from release analysis in Figure 3. The column flotation results are relatively consistent and near the release analysis performance. The samples are being analyzed for total sulfur content to assess the sulfur rejection performance.

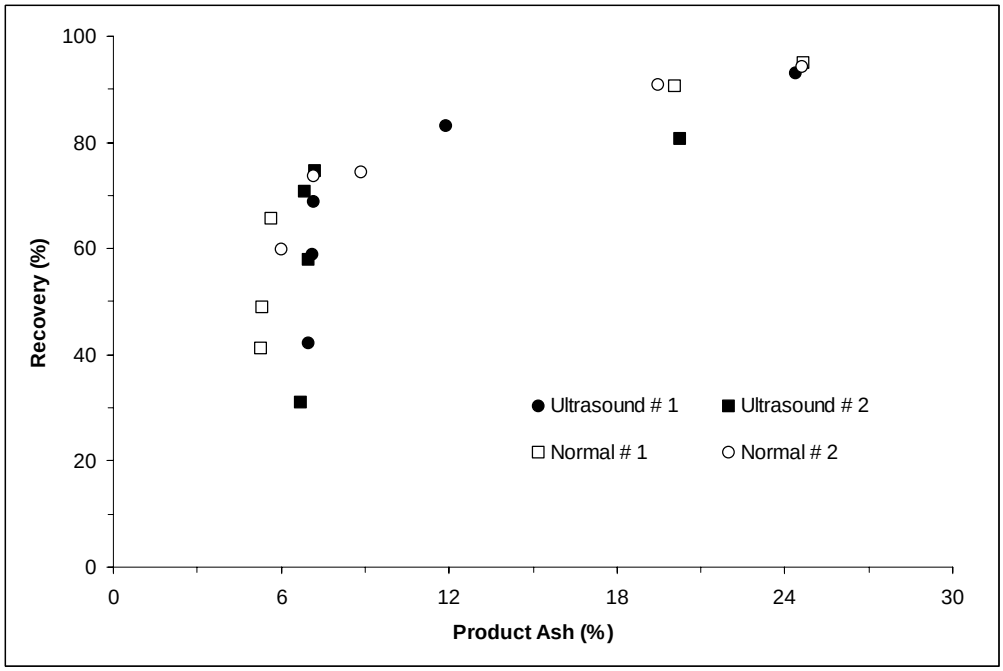

Figure 2. Column flotation data obtained from test with ultrasonic energy (first row) and without it (second row).

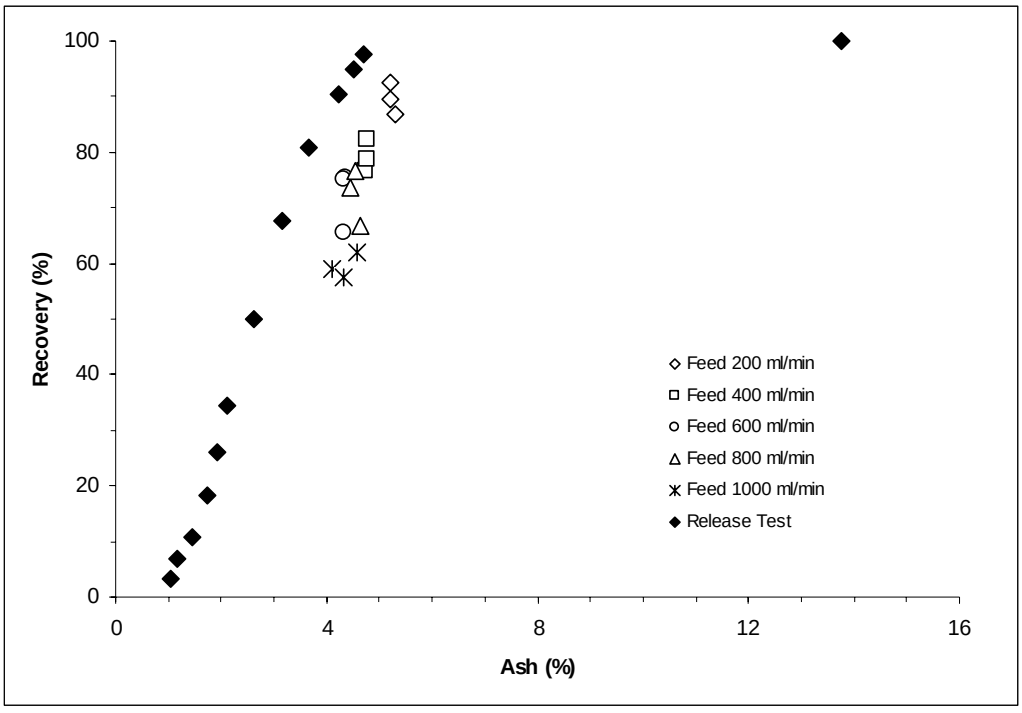

Figure 3. Column flotation and release analysis results for Pittsburgh # 8 sample.

Task 3. External Refluxing for Improved Selectivity

The objective of this task is to evaluate the potential of refluxing a small portion of the froth product to enrich the froth zone thereby improving selectivity as a result of selective detachment of the more weakly hydrophobic, low quality particles. The effort in this task has not been initiated to date.

SUMMARY

The accomplishments achieved to date can be summarized as follows:

1. A graduate research assistant, Mr. Carlos Munoz, has been hired to work on the project as part of his M.S. degree requirements. Mr. Munoz has worked for four years as a Mining Engineer in the copper industry in Chile. However, he had very little flotation experience. As such, a significant amount of time has been devoted to providing knowledge and training in flotation fundamentals and column operation.

2. A commercially available magnetic plastic called 'PolyMag' has been secured in large quantities. Contact angle measurements revealed excellent surface hydrophobicity with an angle of 83^{o}, which is larger than generally realized for most coal and mineral surfaces. Also, the material is easily ground to the required particle size using a hammer mill.

3. Two run-of-mine coal samples have been collected and crushed to the required particle size for the flotation tests, i.e., -65 mesh. The sources include the Hazard No. 4 coal seam and the Pittsburgh No. 8 coal seam. It is expected that selective detachment using the magnetic plastic material or external recycling may be more beneficial for coal in the rejection of sulfur, which is found at high concentrations in the Pittsburgh No. 8 coal seam.

4. Preliminary tests have not provided evidence that the injection of the magnetic plastic or the application of ultrasonic energy into the froth zone improves flotation selectivity on the basis of ash rejection. A more fundamental approach to the test program is needed to evaluate the potential impact and to quantify the potential improvement. Improved sulfur rejection has not been addressed to date but the process samples are currently being analyzed to assess the potential.

FUTURE WORK

Obtain carrying capacity limit for Pittsburgh # 8 sample, run several test at carrying capacity limits with adding magnetic plastic material at different solid concentration rate into

the froth zone. Recover the magnetic plastic material with a magnetic separator and evaluate the impact of adding higher hydrophobic material into the froth zone for ash and total sulfur rejection.

Repeat the same test describe above by using the same clean coal obtained at different feed rates instead of plastic material to quantify the impact of adding the plastic.

Collect a pure coal by obtaining 1.3 float material and pure coal pyrite by gravity separation. Conduct flotation tests on each component separately and as a blend with and without the magnetic plastic material using varying concentration amounts. The effort in the tests will be to quantify the amount of selective detachment that occurs under different solid loadings and quantities of magnetic plastic material.

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PUBLICATIONS/PRESENTATIONS

No publication or presentations have been done yet.

Appendix 7: Engineering Development of a Fine Particle Heavy Medium Separator (VA012)

TECHNICAL PROGRESS REPORT

Contract Title and Number:	Period of Performance:
Crosscutting Technology Development at the Center for Advanced Separation Technologies (DE-FC26-02NT41607)	Starting Date: 6/1/05 Ending Date: 10/31/06

Sub-Recipient Project Title:	Report Information:
Engineering Development of a Fine Particle Heavy Medium Separator	Type: Semi-Annual Number: 1 Period: 10/1/05-3/31/06
Principal Investigators:	Date: 4/30/06
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No subcontracts issued.	Phone: Fax: E-Mail:

ABSTRACT

The objective of this project is to develop an innovative heavy medium separator that can reduce the cost and improve the efficiency of fine coal cleaning. The technology is designed to replace inefficient water-based separators such as spirals and water-only cyclones that are currently used by industry to upgrade 1 x 0.15 mm run-of-mine coal. The new heavy medium separator incorporates novel design features that allow it make sharp separations without the need for costly micronized magnetite. As a result, the new technology can share circulating medium from other circuits, thereby avoiding the expense of installing and maintaining an additional medium circuit. These advantages, together with the low headroom design of the module, make it possible to integrate this technology into an existing plant with minimal retrofit costs. The project tasks will include (i) design and construction, (ii) pilot-scale testing, (iii) field testing, and (iv) flowsheet development.

INTRODUCTION

Background

Heavy medium cyclones (HMCs) have been used for more than 50 years by the mining industry to upgrade a wide variety of raw materials including coal, magnesite, dolomite, diamonds, potash and lead-zinc ores. These inexpensive, high-capacity units utilize centrifugal forces to enhance the separation of smaller particles that cannot be efficiently treated using static density-based separators (e.g., heavy medium vessels and jigs). In the U.S. coal industry, heavy medium cyclones are used in nearly 80% of all coal preparation plants and represent a total installed capacity of nearly 80,000 ton/hr of feed coal. Most of these units treat feed coals in the 50 x 0.5 mm size range (Wood, 1997). More recently, there is renewed interest in using heavy medium cyclones to treat finer coal feeds (i.e., down to 100 mesh) to take advantage of yield gains that may be realized by replacing inefficient water-based separators. Data reported in the literature indicate that a properly configured heavy medium cyclone circuit can provide Ep values that are 3-4 times better than can be achieved using water-based separators such as spirals or water-only cyclones (Moorhead, 1999). Unfortunately, the use of heavy medium cyclones to upgrade fine coal has not been widely accepted by industry since existing designs of heavy medium cyclones require the use of ultrafine (micronized) magnetite in order to efficiently separate fine coal. The ultrafine magnetite is needed to prevent coal losses associated with an internal buildup of middlings that occur due to excessive medium segregation (Wood, 1990). The milling infrastructure required to generate sufficient tonnages of ultrafine magnetite at an acceptable cost is also not currently available. Production reports also indicate that the consumption of ultrafine magnetite is unacceptably high due to the limited effectiveness of conventional magnetic separators in recovering micronized particles. These difficulties have combined to make the use of heavy medium cyclones impractical for treating coal feeds finer than 0.5 mm (Robertson et al., 1997).

Cyclone designers at Krebs Engineers have been working to develop a new heavy medium separator that can be used to effectively treat fine coal. The proprietary technology incorporates novel design features that allow it make sharp separations without the need for costly micronized magnetite. As a result, the new technology can share circulating medium from other circuits, thereby avoiding the expense of installing and maintaining an additional medium circuit. These advantages, together with the low headroom design of the module, make it possible to integrate this technology into an existing plant with minimal retrofit costs.

Objective and Approach

The primary objective of this project is to complete the engineering development of an innovative heavy medium separator that can reduce the cost and improve the efficiency of fine coal cleaning. The technology is designed to replace inefficient water-based separators such as spirals and water-only cyclones that are currently used by industry to upgrade 1 x 0.15 mm run-of-mine coal. The proposed work will include (i) design and construction, (ii) pilot-scale testing, (iii) field testing, and (iv) flowsheet development.

PROJECT TASKS

Task 1 – Design and Construction

Most of the project work performed during the current reporting period focused on the design and construction of a 6-inch diameter prototype separator. To date, technical personnel from Krebs Engineers have provided most of the essential fabricated components necessary to assemble the prototype unit. Additional fabrication work to complete the assembly is currently ongoing in the machine shop at the Virginia Tech. Steps are also underway to set up a pilot-scale test rig at the Virginia Tech off-campus coal testing facility. The test circuit includes a 200 gallon feed medium sump, a variable-flow centrifugal feed pump, associated control/regulation valves, and proportional sample cutters. The construction work and other activities associated with the design, procurement, fabrication, and assembly of the prototype separator and test rig are expected to be completed by the end of the next reporting period.

Task 2 – Pilot-Scale Testing

This task will require the completion of a variety of experimental test runs to evaluate the performance of the prototype separator. This work is expected to begin shortly after the completion of construction and fabrication activities conducted under Task 1. In anticipation of this activity, a simple two-level parametric study has been developed to investigate the effects of the key operating variables. A statistical software package will be used to assist in the formulation of an appropriate test matrix. At present, a total of 30 individual test runs are expected to be conducted (10 runs/seam x 3 seams = 30 runs) using the prototype unit.

Task 3 – Field Testing

No experimental test work or analyses were performed under this task during the current reporting period. This effort will not begin until after the successful completion of all previous tasks.

Task 4 – Flowsheet Development

No engineering work or analyses were performed under this task during the current reporting period. This effort will not begin until after the successful completion of all previous tasks.

SUMMARY

Initial work has begun to design, fabricate and construct a prototype heavy medium cyclone specifically designed for treating fine coal. The work completed to date includes shipping of the necessary components from Krebs Engineers to the Virginia Tech test facility, assembly of these parts with components fabricated at Virginia Tech, and the initial

setup of the associated pilot-scale circuitry necessary to evaluate the new technology. A preliminary test plan has also been developed for future testing of the prototype separator.

FUTURE WORK

Future work will focus on the completion of construction activities and initiation of preliminary shakedown tests for the prototype heavy medium cyclone.

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PUBLICATIONS/PRESENTATIONS

None for the current reporting period.

Appendix 8: Improved Destruction and Control of Residual Flotation Froths (VA014)

TECHNICAL PROGRESS REPORT

Contract Title and Number:	Period of Performance:
Crosscutting Technology Development at the Center for Advanced Separation Technologies (DE-FC26-02NT41607)	Starting Date: 6/1/2005 Ending Date: 10/31/2006

Sub-Recipient Project Title:	Report Information:
Improved Destruction and Control of Residual Flotation Froths	Type: Semi-Annual Number: 1 Period: 10/1/05-3/31/06
Principal Investigators:	Date: 4/30/06
Gerald H. Luttrell and Roe-Hoan Yoon	Code: VA014
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No subcontracts issued.	Phone: Fax: E-Mail:

ABSTRACT

Flotation froths containing large amounts of ultra-fine particles can become excessively stable and create serious handling problems for coal preparation plants. Steps taken by operators to combat these problems, such as lowering the frother dosage, have resulted in large reductions in fine coal recovery and plant profitability. The objective of this project is to develop and evaluate several improved methods for the control and destruction of residual flotation froths. The first phase of the proposed work will focus on a detailed laboratory study of the physical and chemical parameters that impact froth stability. These studies will be followed by in-plant sampling campaigns at several coal plants to establish how frothing agents partition within different circuits and to determine whether modifications to the layout or dilution practices can minimize handling problems. The data obtained from these investigations will be used to develop improved mechanical and chemical methods for froth control/destruction at an industrial plant site. During this reporting period, frother partitioning tests were conducted at an industrial plant site. Pilot-scale testing of a froth evacuation system was also carried out. In addition, several series of lab-scale tests were also conducted to gain a better understanding of the froth stability problem.

INTRODUCTION

Background

Column flotation cells have become widely used in the coal industry as a result of their ability to maintain superior levels of ash removal compared to conventional mechanical cells. Unfortunately, problems associated with the handling of column froths can be a major problem for plant operators. Column cells typically require a relatively high dosage of strong frother to create a froth depth that can properly distribute the wash water and maintain the desired cleaning action. As a result, column froths containing large amounts of ultra-fine (minus 325 mesh) coal generally become excessively stable, creating backup problems in launders and serious handling difficulties throughout the plant in sumps, pumps, thickeners, sprays, etc. Attempts to overcome these problems by selecting weaker frothers or by reducing frother dosages have resulted in unacceptably low recoveries of clean coal.

Several circuit modifications have been adopted by the coal industry to help deal with the froth stability problem. Oversized launders with steep slopes are typically used to minimize the potential for froth backup. Most columns circuits are configured to keep horizontal froth travel distances as short as possible and to provide sufficient vertical head between the column launder and downstream units. Steps are also taken to avoid the need to pump slurries containing large amounts of entrained air. Nearly all new column installations incorporate a de-aeration tank to provide time for the froth to collapse and for air to escape. Downstream dewatering units also have to be modified so that large froth volumes can be accepted. For example, screen-bowl centrifuges are commonly retrofitted with very large feed inlets to minimize flow restrictions for column froths. In addition, most installations find it necessary to add large dosages of expensive defoaming agents to help deal with the froth stability problem. Yet, despite all of these efforts, column froths continue to be a constant source of difficulty for plant operators and a leading cause of poor performance in plants equipped with column cells. One recent study indicated that coal losses attributed to froth handling problems in column circuits cost one eastern U.S. coal producer more than $8 million annually.

Objective and Approach

The objective of this project is to develop and evaluate several improved methods for the control and destruction of residual flotation froths generated by industrial coal flotation plants. Specific tasks to be completed as part of this effort include (i) laboratory studies of physical/chemical parameters influencing froth stability, (ii) quantitative assessments of frother partitioning in industrial coal preparation plants, (iii) evaluation of mechanical methods for froth control/destruction, and (iv) evaluation of chemical methods for froth control/destruction. The work associated with the proposed R&D activities will be carried out by a multidisciplinary team consisting of university personnel from Virginia Tech as well as key industrial personnel from a major eastern U.S. coal company.

PROJECT TASKS

Task 1 – Parametric Study of Froth Stability

The objective of this task is to conduct a variety of fundamental laboratory studies that are needed to identify the key factors that influence froth stability. To date, most of the work performed under this task focused on the construction and setup of an experimental apparatus that can be used to monitor froth height profiles as a function of various test parameters (e.g., particle size, shape, concentration, surface wettability, frother dosage, defoamer dosage, gas rate, etc.). The results obtained from these fundamental tests will be reported in the next technical progress report.

Task 2 – Investigation of Residual Frother Partitioning

The objective of this task is to conduct measurements that provide an indication of (i) the effective frother concentrations in different plant circuits, (ii) how these concentrations are impacted by circulation and dilution streams, (iii) which unit operations are adversely impacted by excessively stable froths, and (iv) the level of severity of the froth stability. In this work, the effective frother concentration was determined by measuring the liquid surface tension of the sampled solutions (after solids removal using a microfilter or centrifuge) and comparing the measured value to a laboratory calibration curve of concentration versus surface tension. Surface tension measurements were initially performed using the du Nüoy ring method and were later compared to those obtained using the Wilhemy plate method. It was found out that due to technical limitations, the du Nüoy Ring Method gave inconsistent results. Thus, it was decided to use Wilhemy plate method for future testing.

Two sets of samples were subjected to surface tension measurements to establish residual frother concentrations. The first series were carried out on samples collected from a laboratory-scale flotation cell. These lab tests were performed in order to check whether the surface tension method can provide the required data. The results obtained from the laboratory experiments are summarized in Figure 1. As expected, the surface tension of the pulp within the flotation cell increased as the frother was depleted during the flotation test run. However, the surface tension values for the froth concentrates were inconsistent and did not follow any expected trend. The relatively high surface tension values for the

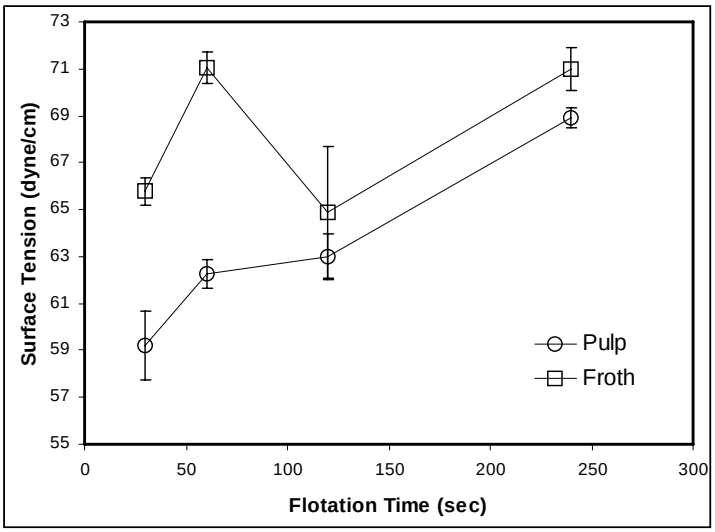

Figure 1. Surface tension measurements for samples from a laboratory flotation machine.

froth products suggest that this method of monitoring the concentrations of frother may not be reliable due to the presence of ultrafine coal particles in the samples.

The second group of samples was obtained from an operating plant (see Figure 2). In the preliminary evaluation, samples that were taken included (i) clarified water from the plant thickener, (ii) feed, concentrate and tailings samples from the two plant columns, and (iii) feed, concentrate and tailings samples from the first and last cells in the bank of plant conventional cells. The results of these measurements are plotted in Figure 3. As can be seen, some of the surface tension values are not as expected. The froth concentrate samples tended to give higher surface tension values which are indicative of lower frother concentrations. This unexpected result is believed to be due to sampling issues in which slurry is collected from the plant and transported back to the lab before the measurements of surface tension can be done. Recent tests show the frother concentration changes during this time due to decomposition and/or by deposition on coal particles in the system. Thus, to counter these negative effects, filtering during sampling via syringe microfilters is going to be performed at the plant site for the next round of in-plant tests.

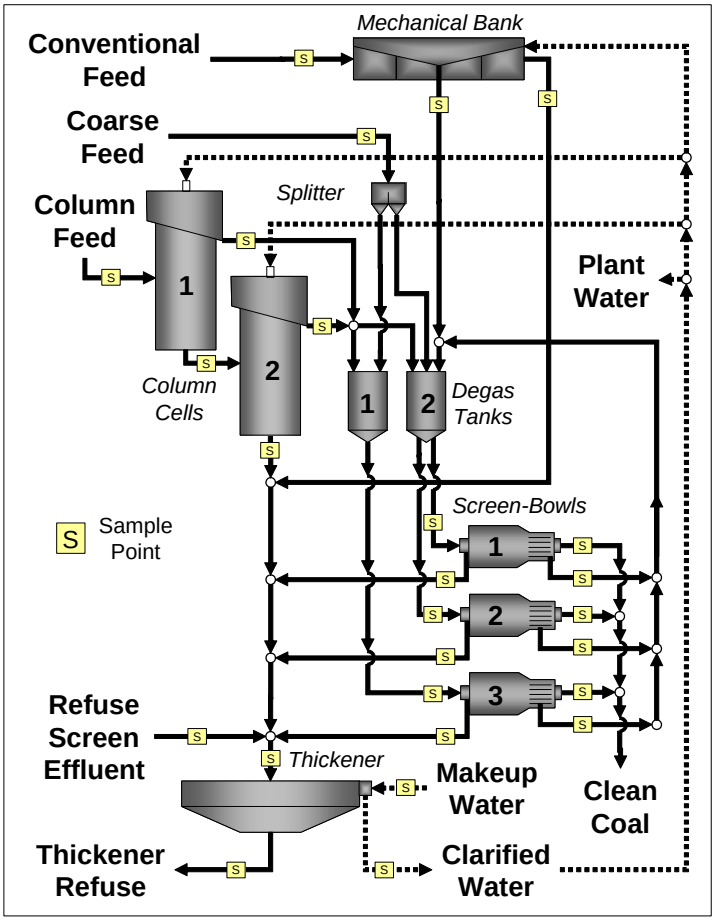

Figure 2. Flowsheet showing sampling points.

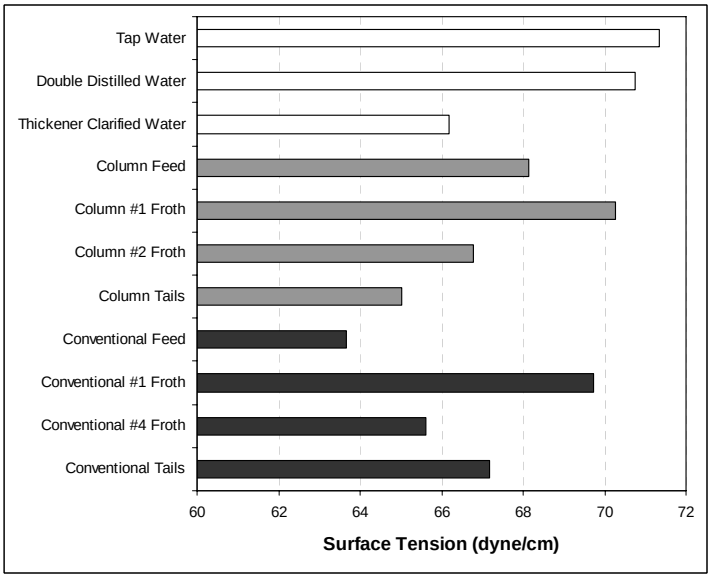

Figure 3. Comparison of plant surface tension values.

Task 3 – Evaluation of Mechanical Control Methods

This task focuses on the evaluation of several mechanical methods for froth destruction and/or prevention. This approach is less costly than chemical control methods and avoids recycled defoamer in the clarified return water that may inhibit flotation performance. The first mechanical method evaluated as part of this task was a froth evacuation system (FES). This method uses a vacuum system to draw froth into a vacuum chamber where entrained air bubbles are expanded or collapsed (see Figure 4). A barometric leg is then used to carry the deaerated slurry to a refuse thickener for disposal. During this reporting period, tests were carried out using a pilot-scale FES at an industrial plant site. Preliminary tests conducted with this unit showed that a larger volume vacuum receiver tank as well as a more powerful vacuum pump is needed to increase throughput. Problems of heavy frothing were also observed in both the effluent and receiver sumps. These problems were solved using paddle mixers to keep the frothing to an acceptable level by agitating the contents. Although several tests were run to date, satisfactory results could not be obtained. Deaerated samples from the receiver tank did not settle after the application of flocculants. To correct this issue, modifications have recently been made to the vacuum receiver tank so that the material is fed to it tangentially to create a cyclonic action to achieve separation of froth and foamy material from rest of the slurry. Testing to evaluate this modification is currently underway.

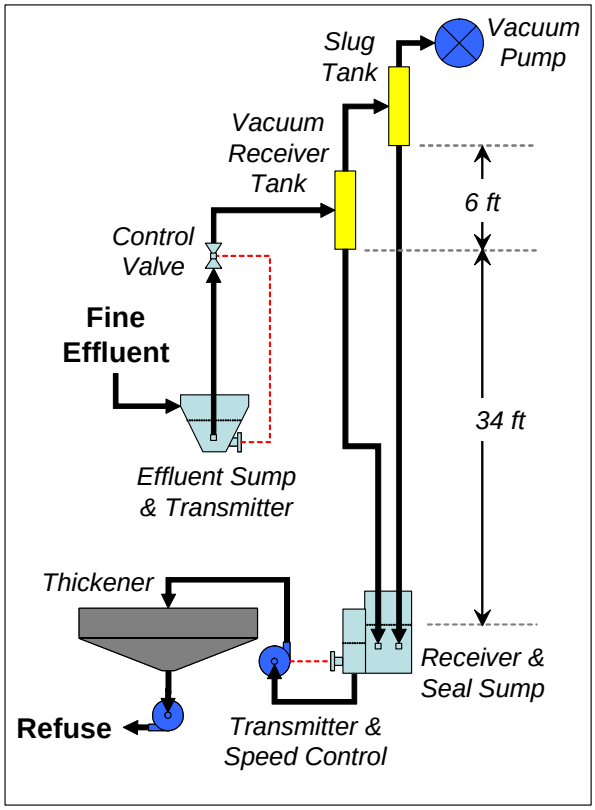

Figure 4. Froth evacuation system (FES).

SUMMARY

During this reporting period, frother partitioning studies and froth evaluation tests were conducted at an industrial plant site. The frother partitioning studies indicate that the samples must be taken in the field to avoid frother decomposition and/or adsorption on coal particles that interfere with the measurements. Preliminary results from the froth evacuation tests indicate that direct evacuation is not by itself capable of deaerating coal flotation froths. Modifications have been made to the test apparatus in an attempt to improve this technique.

FUTURE WORK

During the next reporting period, plant water will be analyzed with the new approach described above for its frother content (surface tension measurements), size distribution, combustibles and ash content and, chemical composition. Froth stability tests will also be carried out to develop a better understanding of the effects of particles size and frother content on froth stability. A modified froth evacuation system will also be examined in more detail.

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PUBLICATIONS/PRESENTATIONS

None are available for the current reporting period.

Appendix 9: Development of a Turbulent Flotation Model and a Computer Simulator (VA015)

TECHNICAL PROGRESS REPORT

Contract Title and Number:	Period of Performance:
Crosscutting Technology Development at the Center for Advanced Separation Technologies (DE-FC26-02NT41607)	Starting Date: 6/1/2005 Ending Date: 10/31/2007

Sub-Recipient Project Title:	Report Information:
Development of a Turbulent Flotation Model and a Computer Simulator	Type: Semi-Annual Number: 2 Period: 04/01/06-09/30/06
Principal Investigators:	Date: 10/01/06
Yoon, Luttrell	Code: VA015-R02
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Subcontractor Address:	Subcontractor Information:
Insert address of subcontractor. If none awarded, insert "No subcontracts issued."	Phone: Fax: E-Mail:

ABSTRACT

In the previous report, CAST developed a model for mineral processing called flotation in turbulent flow conditions accounting for both hydro-dynamical and chemical aspects. Briefly speaking, flotation is a technology separating valuable minerals from the raw materials that is designed to selectively attach hydrophobic particles on the surfaces of air bubbles and collect the concentrate. According to the reported model, the total recovery was expressed by a product of two distinct recovery fractions: one in the pulp region and another in the froth region. However, the latter involved empirical relations rather than analytical. Accordingly, CAST continues to improve the model by describing the interactions occurring in the froth in more analytical ways. However, this is such a challenging task that the current report states only the preliminary stages of complete froth modeling. Finally, the improved flotation model with more analytical froth terms will make significant contributions to enhancing the productivity of mineral processing and other industries of similar applications.

INTRODUCTION

Background

In many industrial processes, foams develop over large tanks that contain liquids. In some cases foams are desirable, while in others they are detrimental to the engineering process. One of the industrial processes is the flotation of minerals. In this process, bubbles are generated in a stirring tank and mixed with ground product. Ore particles are then attached to the bubbles and float to the top forming foam. One of the most important applications is coal cleaning and separation. This specific coal process is efficient because coal particles are hydrophobic and thus attach to the bubbles, and the aggregates float to the top to form froth. Therefore, understanding and prediction of foam processes is important for designing effective mineral processing equipments or controlling the productivity.

In a flotation cell, rising bubbles that reach the pulp/froth interface quickly form a geometrical foam structure made up of polyhedra. Within just a few bubble diameters above the liquid foam interface, foam is practically dry. Dry foam can be defined as the state of foam where the sides of the polyhedra are flat films with very small thickness. These films are called lamellae, and the edges of the polyhedra are tubes with tricuspid cross-sections called Plateau borders (PB). In dry foam, the liquid is contained mostly in the Plateau borders and small amounts of surfactants are enough to arrest the fluid velocity on the walls of the lamellae and the PBs. A dry foam structure is thus equivalent to a complex network of solid pipes, except that these pipes can expand and contract depending on the wetness of the foam. Some authors (Goldfarb *et al*.,1987; Leonard and Lemlich,1965; Verbist et al.,1996) neglect the viscous losses along the junctions and arrive at simple equations that govern foam drainage. More advanced modeling has also been achieved (Neethling *et al*.,2002; Koehler *et al.*,2000) taking into account losses in the junctions. But most of these solutions have been limited to ideal situations that neglect the rising of the foam and its coarsening. Being far from this ideal situations and ,in addition, subject to chemical effects by such factors as surfactants, mineral particles and so on, the understanding foams/froths in mineral processing is daunting but will make great contributions to mineral processing and related applications once it is done.

Objective and Approach

The big picture of this project is obtaining a complete flotation model under turbulent conditions. As one of the several preliminary stages to this final goal, CAST plans to improve the previous flotation model by enhancing the analytical modeling of foam for the corresponding period of performance.

PROJECT TASKS

Drainage of liquid is the most common physical phenomena observed in foams/froths. Therefore, CAST continues the work with deriving a general mathematical drainage model that accounts for coarsening and pressure changes along the foam column.

Then the proposed model is simulated by numerical solutions. The details and interim results of the model development are discussed in the following sections.

Task 1- Development of a Model

Analytical Modeling of Drainage

Considering liquids in a foam as flowing through the networks of plateau borders, the conservation of fluid mass yields simple relationship between the cross-section of the Plateau Borders (PB), *A*, and the mean velocity in a PB, *u*:

$$\frac{\partial A}{\partial t} + \frac{\partial}{\partial x}(Au) = 0 \qquad (1)$$

Here, area *A* represents the wetness ratio of foam as described later and *x* is the distance in the vertical direction downward from at the free surface of the foam column. This is the basis on which other simple models of drainages were developed (Goldfarb *et al*.,1987; Verbist *et al*.,1996), and those models resemble the Berger's equation in their non-dimensionalized forms. Their characters are similar to boundary-layer equations and can be solved numerically by methods established many years ago (Telionis, 1981). However, Verbist *et al*. (1996) derived an analytical solution of this equation assuming that the area (*A*) profile along the foam depth (*x*) has the form of a solitary wave. But the nature of a propagating wave does not conform to a realistic initial condition because it could be either wet or dry, and feasibly uniform. Therefore, those models are not appropriate to be incorporated with the flotation model.

Extension of the Analytical Model

Equation by Verbist *et al*.(1996) is based on the assumption that foam consists only of a network of tubes. This may be acceptable in the case of very dry foams where the sizes of junctions are negligible. But it may no longer be a good assumption if the foam contains more fluid. The fluid contained in the junctures, *i.e*. the vertices of the polyhedra and the corresponding friction losses must be considered. Whether losses through the vertices or PBs, dominates the drainage is still controversial but Neethling *et al*.(2002) claim that both play important roles. Accounting for the losses through the vertices, a more generalized drainage equation is expressed in terms of liquid fraction ε. ε, defined as the ratio between the total PB area and the cross-sectional area of foam column, represents the wetness of the foam because the the PB area is assumed to be fully occupied by liquid contents. If there is no significant change in temperature along the foam column, the product of gas pressure (*p*) and volume of a bubble cell (*V*) stays constant neglecting the diffusion of gases. Finally, accounting for all those, one obtains the drainage equation as follows.

$$\frac{\partial \varepsilon}{\partial t} + \frac{\partial}{\partial x}\left(\frac{\varepsilon \rho g}{k\mu} + \frac{\varepsilon \nabla(-(pV)_{top}/(\frac{4}{3}\pi r_b^{\,3}) + \gamma / r)}{k\mu} \right) = 0 \qquad (4)$$

Where *r* is the radius of curvature of PB, γ is the liquid surface tension, and k is the pressure drop coefficient both through PBs and vertices. As one can see, this equation accounts for

variations in the bubble size r_b. Following the same approach with Verbist *et al*.'s (1996). The nondimensional form of Eq.(4) is as follows.

$$\frac{\partial \alpha}{\partial \tau} + f_1 \frac{\partial}{\partial \xi}\left(\frac{\alpha}{\kappa} + \frac{\alpha}{\kappa}\frac{\partial}{\partial \xi}\left(\frac{-C_1}{\beta^3} + \frac{1}{0.4\delta} \right) \right) = 0 \qquad (5)$$

Where the Greek letters represent the non-dimensional versions of corresponding parameters in Eq.(4), f_1 is a constant defined as $150/C_v$, C_v representing the pressre drop coefficient through foam vertices. β and δ means r_b and r nondimensionalized by the chanracteristic length respectively. The other constant C_1 is determined by fluid properties ρ, γ and the value of pV at the top of the foam. It should be noted that Eq.(5) takes the same form with the model by Verbist *et al*. when the assumptions of dry foams with monodisperse bubbles are taken.

Task 2- Simulation and Analysis

In the beginning, the ideal model by Verbist *et al*. had been numerically solved and compared with its analytical solution. Both solutions showing good agreements, CAST formulated similar numerical solutions of Eq.(5) yet with monodispersed foam, *i.e*. β =constant. Here, κ is a nondimensional expression of k given by the following relation.

$$\kappa = \left(\frac{3\Phi}{\delta^2} + \frac{4.178(1-0.418\Phi)}{\delta\beta}(1-\varepsilon)^{1/3} + \frac{6.806(1-1.588\Phi)}{\beta^2}(1-\varepsilon)^{2/3} \right) \qquad (6)$$

where Φ is defined as the ratio of the pressure drop coefficient in the PB and in the vertex ($\Phi = C_{PB}/C_V$).

Simulations were run for cases with several values of Φ. CAST has found that when the ratio is getting larger than 5, and with C_V as small as 5, the wetness profile looks similar to the profile by Verbist *et al*. Φ values larger than 6 gave frequent errors that stopped the calculation. Therefore, the current work mostly shows the results of Φ values of order 10^0 or closer. N_{PB} was assumed to be 30 when the monodisperse bubbles have a diameter of 5 mm and the foam column has a diameter of 3.4 cm.

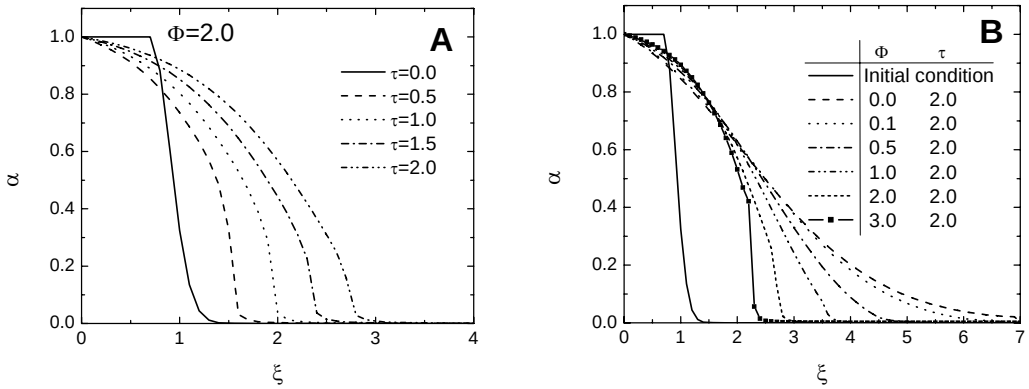

Fig.1 A) Propagation of wetness with time with f_1=5. B) Wetness profile change according to C_{PB}-C_V ratio change. Given f_1=5, the results for the same instance (τ=2) are shown.

Fig 1. briefly describes the findings by the present drainage model. Given the initially dry foam with liquid dropping at the top (ξ=0), the wetness propagates as shown in Fig.1 A. This resembles the wave-like profiles of the ideal model, but with the upper region draining retarded comparing with the lower region. Fig.1 B shows that the profile changes its slope with various C_{PB}-C_V ratios. As the ratio(Φ) increases, the profile slope tilts up more indicating that the lower foams drain slower while the upper foams drain a little faster. What this figure means also is that PBs are more important in wet foams whereas vertices are in dry foams. Therefore, Fig 2-B helps one determine in what position the distinction between PB drainage and vertex drainage can be made at a certain instance.

SUMMARY

An analytical drainage model has been derived that incorporates liquid flow through both the PBs and PB junctions. Applied a simple boundary and initial conditions, the simulation results on this model showed that drainage is more likely to occur through PBs when the foam is wet, while it is through vertices with dry foams. The findings by this model may be useful in controlling the stability of foams and froths hence the productivity of related natural resources.

FUTURE WORK

The simulation should be done with more realistic boundary conditions (such as coagulations and foam growing) and various initial conditions (free drainage or forced drainage) accompanied by some experimental validations. In addition, associating the effects by particles and surfactants in any manner will also be necessary for an advanced model. Another, the contribution of liquid films in drainage is controversial but may be accountable in the future work. Then the complete drainage model will be able to be combined into the flotation model.

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Appendix 10: Novel Surfactants as Collectors for Froth Flotation (VA017)

TECHNICAL PROGRESS REPORT

Contract Title and Number:	Period of Performance:
Crosscutting Technology Development at the Center for Advanced Separation Technologies (DE-FC26-02NT41607)	Starting Date: 6/1/2005 Ending Date: 10/31/2006

Sub-Recipient Project Title:	Report Information:
Novel Surfactants as Collectors for Froth Flotation	Type: Semi-Annual Number: 2 Period: 4/1/06-8/31/06
Principal Investigators:	Date: 9/30/06
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No subcontracts issued	Phone: Fax: E-Mail:

ABSTRACT

The synthesis of two homologous series of two-tailed, tricarboxylate amphiphiles has been achieved. All compounds have been fully characterized by the standards of organic chemistry. The compounds are soluble in water as tris(triethanolammonium) salts at a concentration of 1×10^{-3}M or greater. In addition, attaching a tricarboxylate group to polymers that have hydroxyl end groups has been achieved. These modified polymers readily replace oleic acid on the surface of iron nanoparticles. These new materials offer several possibilities for applications in separations of minerals and a new direction for the project.

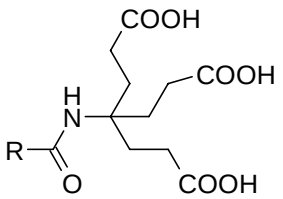
INTRODUCTION

Background

Froth-flotation separation is the most widely used unit process in the minerals processing industry with nearly 100,000 tons of mined ores and coal being floated daily.(Fuerstenau, 1999) Selective hydrophobization of mineral particles by collectors (surfactants) enables separation from the gangue; the hydrophobized particles “attach” to microbubbles(Yoon, 2000) and float to the top of the slurry. One key parameter is the surface charge of the mineral. The adsorption of collectors occurs at specific sites on the mineral surface; knowledge of the surface properties (zeta potential, point of zero charge)(Fuerstenau and

Pradip, 2005) is crucial for designing useful collectors. The strength of the hydrophobic force(Pazhianur and Yoon, 2003) that creates the attachment of the particle to the bubble is another key parameter in designing useful collectors. Collectors that are designed to optimize both hydrophobicity and absorption at specific surface sites can improve both efficiency and selectivity in froth flotation. From the design viewpoint, an optimal collector has a head group to provide the functional groups that attach to the surface and a tail group that provides hydrophobicity.

A novel approach to the design of collectors involves supramolecular preorganization in the head group (polar part) and in the tail group (hydrophobic part) to improve the packing density of the adsorption layer on the mineral particles.(Müller et al., 2005) Improving the packing density should increase the hydrophobicity of the modified surface. A recent report (Müller et al., 2005)describes flotation studies with three types of oligofunctional surfactants—two feature geometrically constrained, preorganized structures and the third has a dendritic structure. Our studies(Williams et al., 2005) of the interactions of dendritic amphiphiles with surfaces show that homologous, single-tailed, long-chain alkyl dendrons **1(n)** with three carboxyl groups form homologous thin films on silver oxide surfaces. Our observations demonstrate that assemblies of these molecules should make hydrophobic coatings. The uniqueness of this homologous series is that contains very long alkyl chains of 19 and 21 carbons, derived from icosanoic (arachidic) and docosanoic (behenic) acid, respectively.



1(n), R = *n*-C_nH_{2n+1}
n = 13, 14, 15, 16, 17, 19, 21

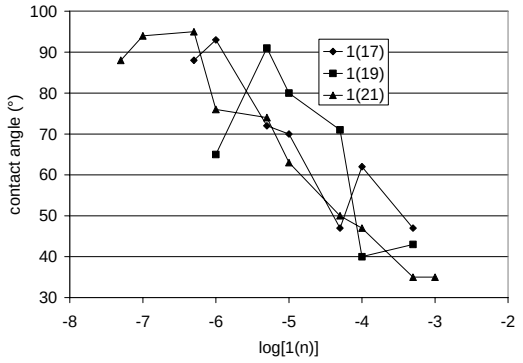


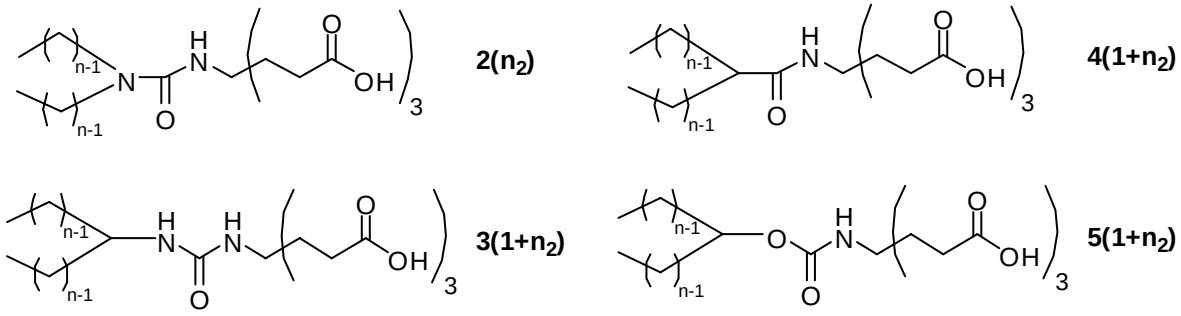
Figure 1. Contact Angles of **1(n)** absorbed on apatite as a function of concentration.

The head group, when neutralized with triethanolamine, is sufficiently hydrophilic to enable good aqueous solubility of the longest chain. The three carboxylates offer and strong binding to a surface because of multiple attachments. Preliminary results (Figure 1) show that **1(21)** produces, at concentrations 1×10^{-7} M, strongly hydrophobic coatings (contact angles > 90°) on an apatite.

Objective and Approach

We propose to synthesize four homologous series of three-headed, two-tail amphiphiles—**2(n_2)**, **3(1+n_2)**, **4(1+n_2)**, and **5(1+n_2)**,. The design idea for these series is to produce the amphiphiles with the same number of carbons as the respective single-tailed amphiphiles. Our hypothesis is that the two-tail amphiphiles will make a more hydrophobic surface because the packing density of the chains has increased compared to single tail amphiphiles. The validation of the hypothesis will occur if the contact angle of a hydrophoblized surface is greater for a two-tail amphiphile than a single-tail amphiphile when the concentrations of

both amphiphiles are equal. The ultimate goal of the project is to find the amphiphile that gives a contact angle >90° with the smallest concentration.



In report VA017-01, we described the syntheses (Figure 2) that began with ther reaction of Weisocyanate™(Newkome et al., 1998) and two-tail amines. The reaction isocyanate occurred at room temperature in good-to-high yields (step i) of triesters (not shown). Formolysis of the trimesters (step ii) produced the triacids—**2(n$_2$)**, where n=6–12 and **3(1+n$_2$)**, where n=6-12—in good yields of recrystallized products. All compounds were fully characterized by the standards of organic chemistry. The compounds were soluble in water as tristriethanolammonium salts at a concentration of 1×10^{-3} M or greater.

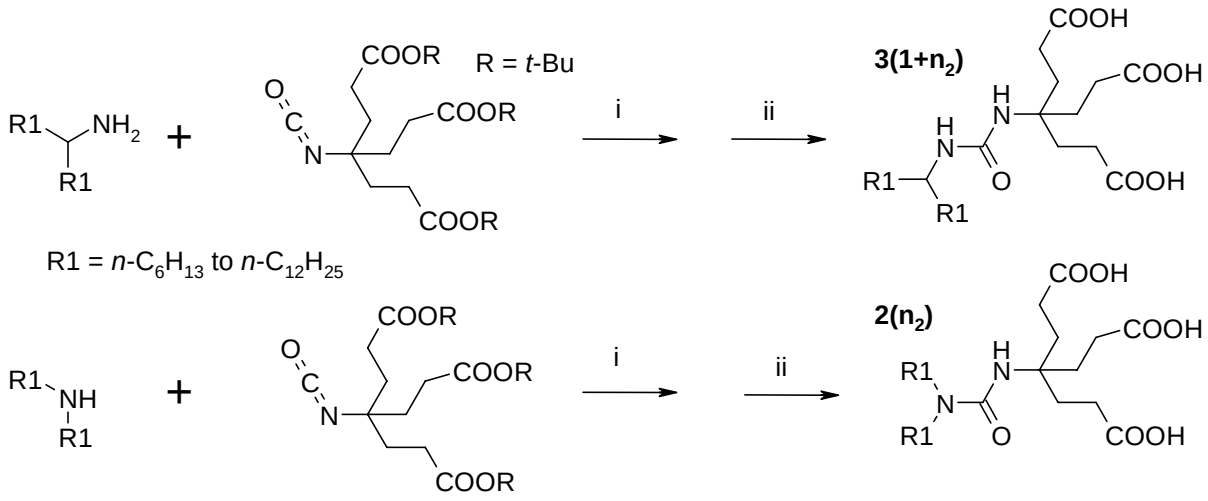


Figure 2. Reagents and conditions: i. NEt_3, CH_2Cl_2, rt, 18 h; ii. HCOOH, rt, 48 h

PROJECT TASKS

In the past 6-month period, we synthesized two additional homologous series (Figure 3) of two-tail, tricarboxylate amphiphiles, **4(1+n$_2$)** and **5(1+n$_2$)**, in good yields. The first series, **4(1+n$_2$)**, required Behera's amine (Newkome et al., 1991) and acid chlorides. The reaction occurred readily at room temperature in the presence of a base to give the triesters. Formolysis of the triesters (step ii) produced the triacids—**4(1+n$_2$)**, where n=6–10—in good yields of recrystallized products. The second series, **5(1+n$_2$)**, required Weisocyanate™(Newkome et al., 1998) and two-tailed alcohols. The reaction occurred readily in hot triethylamine to give the triesters with no detectable side products. Formolysis of the triesters (step ii) produced the triacids—**5(1+n$_2$)**, where n=6–12—in good yields of recrystallized products. All twelve new compounds were fully characterized by the standards

of organic chemistry. The compounds were soluble in water as tristriethanolammonium salts at a concentration of 1×10^{-3} M or greater.

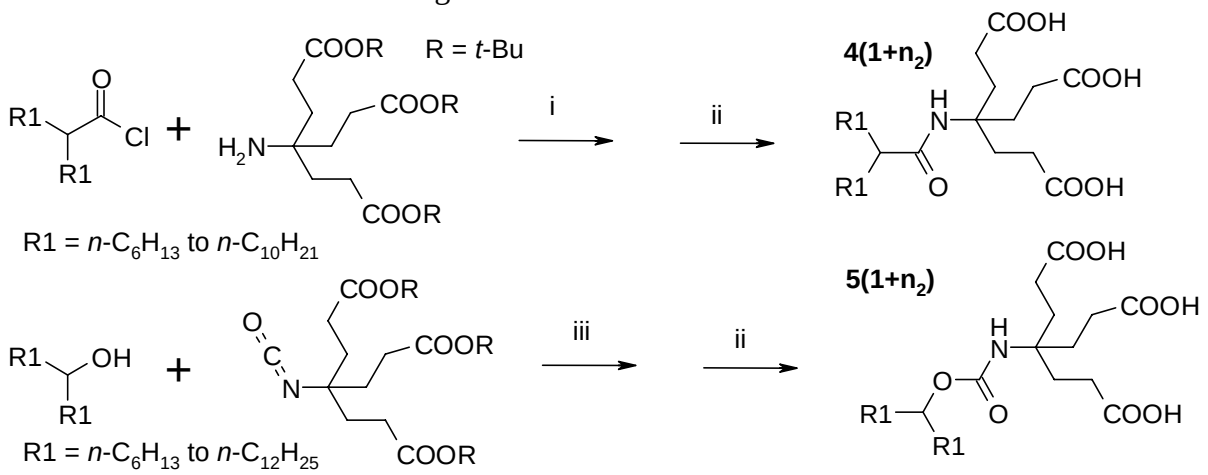


Figure 3. Reagents and conditions: i. NEt_3, CH_2Cl_2, rt, 18 h; ii. HCOOH, rt, 48 h; iii. NEt_3, CH_2Cl_2, 95 °C, 18 h;

In collaboration with Professor Alan Esker (Virginia Tech, Chemistry), we explored the possibility of using the methods for the **5(1+n$_2$)** series for modifying polymers that have

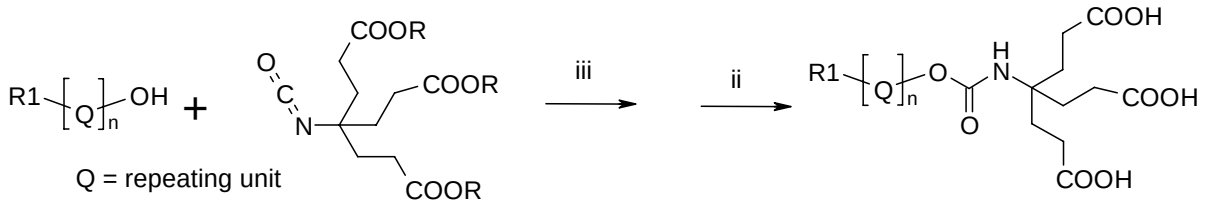


Figure 4. Reagents and conditions: i. NEt_3, CH_2Cl_2, rt, 3 d; ii. HCOOH, rt, 48 h; iii. NEt_3, CH_2Cl_2, 95 °C, 18 h;

hydroxyl end groups. The reaction of Weisocyanate™ with these polymers occurred in high yields in hot triethylamine. Formolysis of the triesters yielded the triacids with no apparent degradation of the polymer. We modified three such polymers with low and medium molecular weights. For proprietary reasons, the exact structures of the polymers are not disclosed.

In a experiment to test the ability of these polymers to bind to iron nanoparticles, we mixed the polymers and oleate-coated nanoparticles in a solution. After the solvent was removed we measured the size of the nanoparticles by dynamic light scattering (Figure 5). The increase in size of the nanoparticles demonstrated that the polymer has replaced the

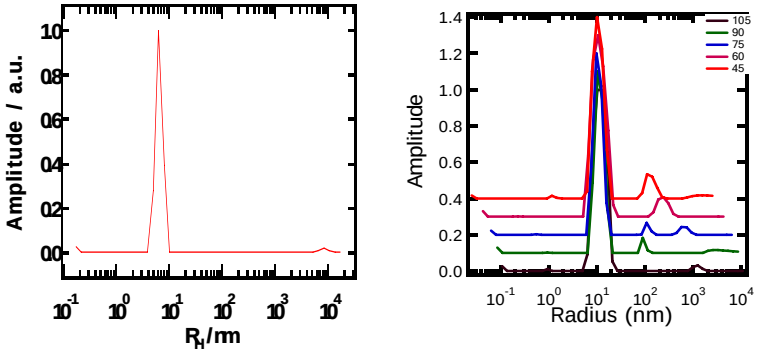


Figure 5. Distribution of nanoparticles by light scattering. (left) Oleate-coated nanoparticles with a mean radius of ~7 nm. (right) polymer-coated nanoparticles with a mean radius of 10 nm.

oleate coating. In a control experiment, the mixing unmodified polymer and oleate-coated nanoparticles did not change the size of the nanoparticle.

SUMMARY

We made twelve new compounds that have been fully characterized. The lowest member of the series is R1 = C_6H_{13}; this means that the two-tail amphiphile has 13 carbons in **4(1+n_2)** and 13 carbons in **5(1+n_2)**. Additional members of the **4(1+n_2)** series have 15, 17, 19, and 21 carbons, respectively; those of the **5(1+n_2)** series have 17, 19, 21, 23, and 25 carbons, respectively. Using the methods develop for the series, we modified the hydroxyl end-group of polymers. These modified polymers bound to iron nanoparticles more strongly than oleic acid; the unmodified polymer did not bind to the nanoparticles.

FUTURE WORK

We shall attempt to measure the contact angles on apatite and calcite of all four series as a function of concentration. We shall modify hydroxy end-group polymers that are hydrophobic and test their ability to coat nanoparticles and surfaces.

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PUBLICATIONS/PRESENTATIONS

None to report this period.

Appendix 11: Alternative Materials for Dense Medium Separations

(KY004)

TECHNICAL PROGRESS REPORT

Contract Title and Number:	Period of Performance:
Crosscutting Technology Development at the Center for Advanced Separation Technologies (DE-FC26-02NT41607)	Starting Date: Ending Date:

Sub-Recipient Project Title:	Report Information:
Alternative Materials for Dense Medium Separation	Type: Semi-Annual Number: 2 Period: 04/01/06-9/30/06 Date: 10/10/06 Code: KY004-R02
Principal Investigators: **Professor Rick Honaker**	
Contact Address: University of Kentucky 234B Mining and Mineral Resources Lexington KY 40506	Contact Information: Phone: (859) 257-1108 Fax: (858) 323-1962 E-Mail: rhonaker@engr.uky.edu
Subcontractor Address:	Subcontractor Information: Phone: Fax: E-Mail:

ABSTRACT

Various materials have been collected and evaluated as potential alternatives to magnetite in dense medium (DM) processes. A reference magnetite with 95% passing 325 mesh was obtained and characterized. Medium stability and separation performance achieved when using the reference magnetite was evaluated in a 6-in DM cyclone circuit treating ¼-in x 28 mesh Coalberg coal. The results obtained from using the reference magnetite were used as a benchmark to assess the potential of the alternative materials.

The alternatives materials evaluated to date include a coarse magnetite source for high-density separations, steel slag and -100 mesh sand. The sand was used to provide a preliminary assessment of the potential of using the coarser particle size fractions in flotation tailings as a potential dense medium material. Unexpectedly, the coarser sand material provided better stability at medium density values of 1.50 and 1.60 RD. This finding may be due to a higher degree of hindered settling and elevated medium viscosities as a result of a higher particle population. The separation efficiency achieved using the sand material was nearly equal to that obtained when using the reference magnetite at a medium density of 1.5 RD and decreased to a slightly inferior level at a medium density of 1.6 RD. At 1.5 RD, an organic efficiency of about 98% was achieved using the sand-based medium. These results imply that the use of the coarser reject material in the fine circuit of a preparation plant could provide an effective, low-cost medium. A test program performed on column flotation tailings material will be performed in the next reporting period.

BACKGROUND

Dense medium processes are used to clean over 50% of the washed coal worldwide. Ultrafine magnetite is added to water to form the dense medium. Due to inefficiencies in the recovery process, typical magnetite losses equate to 1 to 2 lbs/raw ton. In the U.S., a major impact on the magnetite source occurred recently as a result of the closure of an iron ore mine in Missouri. As a result, the current magnetite supply is imported from South America, which has significantly elevated the cost. A new source of magnetite can be fine sand. Physical properties of fine sand can be compared to flotation rejects. Slight modification of flotation reject can potentially be an alternate source of DMS material. With no cost involved in material acquisition, fine sand can be used as an alternative to magnetite. Though, stability problems are not encountered at high medium densities, the high surface area may result in viscosity effects at elevated medium densities that tend to negatively affect separation performance.

PROJECT OBJECTIVES

The goal of the project was to evaluate the potential of using an alternative source of magnetite for the cleaning of U.S. coal.

The objectives of the project are i) to evaluate alternative materials that could be economically used as a substitute for the traditional magnetite in dense medium processes, ii) to develop and evaluate a process in which fine waste material may be used as whole or part of the material needed for adjusting medium density and iii) to provide an excellent educational experience for a graduate student that can be easily translated to industrial application.

PROJECT TASKS

Test Program

A series of dense medium cyclone tests were conducted using a 15-cm (6-in) diameter Krebs unit that was installed in a closed-loop circuit as shown in Figure 1. The test program involved two separate phases. In the first phase, the objective was to evaluate the relative stability of each material in a suspension over a range of medium densities (1.3 – 1.6 R.D.) and feed inlet pressures (2.5 – 10 psi). The stability of a dense medium produced using grade-B conventional magnetite was compared to that provided by -100 mesh fine sand in this report.

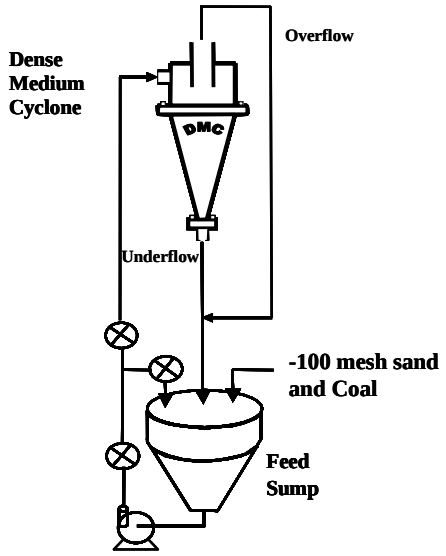

Figure 1. Schematic of the test circuit

The cyclone circuit was constructed as a closed-loop system consisting of a variable-speed motor, centrifugal pump and sump, which has been installed with bafflers to ensure uniform mixing and a pressure gauge. For these tests, the vortex finder and apex diameters were 6.4-cm (2.5-in.) and 4.4-cm (1.75-in), respectively.

The goal of the test program performed during this reporting period was to evaluate the cleaning performances provided by -100 mesh fine sand suspensions when treating 6.4 mm (¼-in) x 28 mesh Coalberg coal collected from preparation plant feed in West Virginia. In these tests, the feed pressure was varied within a range of 5 - 10 psi. Typical plant medium densities of 1.5 and 1.6 RD were investigated, which provided a recovery-grade relationship from sample analysis data generated from the samples collected from each process stream. The samples were also subjected to washability analysis to generate the data needed to quantify critical separation efficiency variables such as the separation density and probable error.

For each test, relative density of the 100 mesh fine sand-water suspension was adjusted to the desired value in the circuit feed sump. After achieving the desired density based on a Marcy density scale, the coal sample was added to the medium in the amount equivalent to a medium-to-coal ratio of about 4:1. The coal and dense medium were pumped to the DMC at a rate that provided a range of 7.5 – 10.0 psi inlet pressure. The slurry was circulated in bypass for at least 5 min to ensure adequate mixing. A feed sample was taken from the bypass discharge at the beginning of each test. The bypass valve was used to adjust the desired pressure. Samples of the underflow and the overflow streams were then taken simultaneously.

Data Analysis

The partition values were calculated from the washability analysis by

$$PN_{ji} = \frac{p_{ji}}{p_{ji} + t_{ji}} \tag{1}$$

where PN_{ji} is the weight fraction of feed coal in relative density interval j that reports to the clean coal for size interval i, p_{ji} and t_{ji} are the weight fractions of clean coal and refuse material in relative density interval j for size interval i, and p_i and t_i are the weight fractions of clean coal and refuse material in size interval i. The clean coal yield was calculated by

$$Y = \frac{f - t}{c - t} \tag{2}$$

where f, t, and c are the ash values of the feed, refuse, and clean coal streams, respectively. Other functions have been used to fit partition data for coal preparation devices. The logistic function has been shown to fit conventional dense-medium cyclone data and that from fine coal separations. This function is given as

$$PN'_{ji} = \frac{1}{1+\exp\{(1.9086/Ep_i)(\rho_{ji}-\rho_{50i})\}} \quad (3)$$

where ρ_{50i} is the relative density corresponding to a partition value of 0.5 for size interval *i*, and ρ_{ji} is the mean relative density for relative density interval *j* for size interval *i.* The probable error, Ep for size interval i is defined as

$$Ep = \frac{\rho_{25} - \rho_{75}}{2} \quad (4)$$

where ρ_{25i} and ρ_{75i} represent the relative densities that correspond to partition values of 0.25 and 0.75 on the partition curve for size interval i.

Task 1: Sample Collection and Characterization

Coal Sample: The raw coal sample was collected from a West Virginia coal preparation plant operated by Arch Coal. The plant processes coal from the Coalberg seam, which has a low Hardgrove Index of around 45. The low index value indicates a high degree of resistance to breakage, which is an important characteristic for the test program due to the recirculation of the slurry as shown in Figure 1. A particle size analysis provided in the first project report found that the weight distribution was fairly evenly split in the size fractions between 6 mm (¼-in) and 28 mesh. The ash content was also well distributed with an average value of 36.12%. The sample has a low sulfur content of 0.68%.

A washability analysis was performed on the nominal 6.4 mm (¼-in) x 28 mesh Coalberg coal. As shown in Table 1, nearly 17% of the coal has density between 1.4 and 1.6 RD, which reflects the difficult cleaning nature of the coal. A relatively large amount of material (i.e., 12%) is present in the 1.60 x 2.00 RD fraction. The amount of material in the middle density fractions is significant for the project since the larger mass will provide more accurate partition curves and, thus a high quality assessment of the separation efficiency parameters.

Table 1. Washability data for the 6.4 mm (¼-in) x 28 mesh Coalberg coal.

Specific Gravity Fractions	Incremental		Cumulative Float		Cumulative Sink		Recovery (%)
	Weight (%)	Ash (%)	Weight (%)	Ash (%)	Weight (%)	Ash (%)	
1.30 float	26.95	3.03	26.95	3.03	100.00	33.17	39.10
1.30 x 1.40	21.39	10.04	48.33	6.13	73.05	44.29	67.89
1.40 x 1.50	6.51	21.06	54.84	7.90	51.67	58.47	75.57
1.50 x 1.60	10.15	30.62	64.99	11.45	45.16	63.86	86.11
1.60 x 2.0	11.99	49.97	76.98	17.45	35.01	73.49	95.09
2.0 sink	23.02	85.74	100.00	33.17	23.02	85.74	100.00
Total	100.00	33.56					

Sand and Reference Magnetite: The fine sand was obtained from Belleview Sand and Gravel, Inc. located in Petersburg, Kentucky. The plant processes nominal sand (fine and coarse), pea gravel and crushed gravel for construction and other purposes. Fine sand was collected and transported in drums. After returning to the lab, the sand sample was wet screened at 100 mesh. The particle size distribution of the -100 mesh sand used in the dense medium experiments is provided in Table 2.

A sample of commercially available B-grade magnetite was obtained from Akers Magnetite Inc. in Kenova, West Virginia. The particle size distribution of the reference magnetite is provided in Table 2.

Table 2. Particle size distributions of the -100 mesh sand and grade B conventional magnetite as determined by wet screening.

Particle Size (US Mesh)	Sand Weight (%)	Reference Magnetite Weight (%)
+100	0.26	0.00
100 x 200	48.85	0.50
200 x 325	29.48	4.95
325 x 400	6.34	7.04
400 x 500	6.83	13.83
- 500	8.24	73.68

.Task 2: Magnetic Fly Ash Evaluation

During the reporting period, the recovery of magnetic material from fly ash has been performed using a spiral concentrator and magnetic separator. Upon collecting a sufficient amount of material, the magnetic fly ash component will be evaluated in the same manner as described for the sand material in this report.

Task 3: Coarse Magnetite Evaluation

The results obtained from the evaluation of coarse magnetite were reported in the first semi-annual report. However, additional tests are currently being performed to evaluate the potential of using the coarse magnetite for high density separations up to 1.9 RD. The results will be presented and discussed in an upcoming report.

Task 4: Autogenous Medium Evaluation

In an effort to obtain a preliminary assessment for the potential of using the fine reject from a preparation plant as dense medium material, -100 mesh sand was prepared and evaluated in the dense medium circuit. The performance achieved with the sand based medium was compared with that realized from the use of the reference magnetite. Based on the success of the sand test program, the evaluation of fine coal tailings material will be initiated during the next reporting period.

Medium Stability:

Medium stability was evaluated by measuring the difference in the density of the overflow and underflow streams under a range of inlet pressures in the absence of coal. As shown in Figures 2 - 5, the suspension developed by the -100 mesh sand sample was relatively stable under all feed pressures and medium densities. In fact, the sand suspension proved to be more stable than the reference magnetite.

Separation Performance Comparison:

The separation performances achieved from the use of the reference magnetite and -100 mesh sand are compared in Figure 6 and Table 3. When using a 1.50 RD medium density, the -100 mesh sand provided a very good separation performance that was nearly equal to that obtained from the reference magnetite. The actual separation density and thus the density offset realized with the sand medium was slightly lower than that obtained from the reference magnetite, which may explain the slightly lower product ash content. The recovery and yield values were essentially equal as well as the organic efficiency. However, the probable error value indicates a 60% lower efficiency than that achieved by the reference magnetite, which may be a result of an elevated viscosity in the sand-based medium. When the medium density was increased to 1.60 RD, the effect on efficiency was even more noticeable as indicated by 1) a drop in yield while increasing product ash content, 2) a decrease in the organic efficiency and 3) an increase in the Ep value. The performance decline occurred despite an improvement in medium stability and a decrease the density offset.

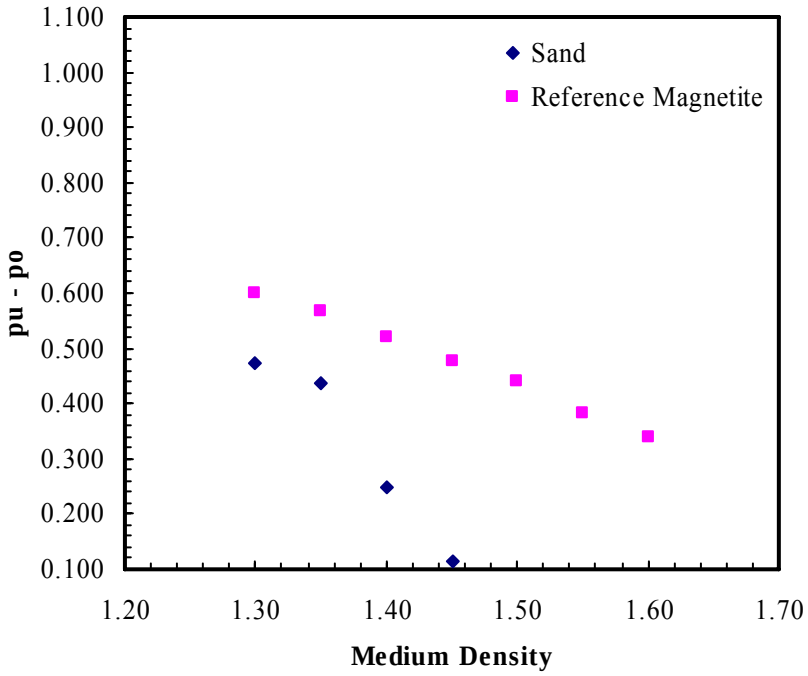

Figure 2. Suspension stability comparison between sand and reference magnetite at an inlet pressure of 2.5 psi.

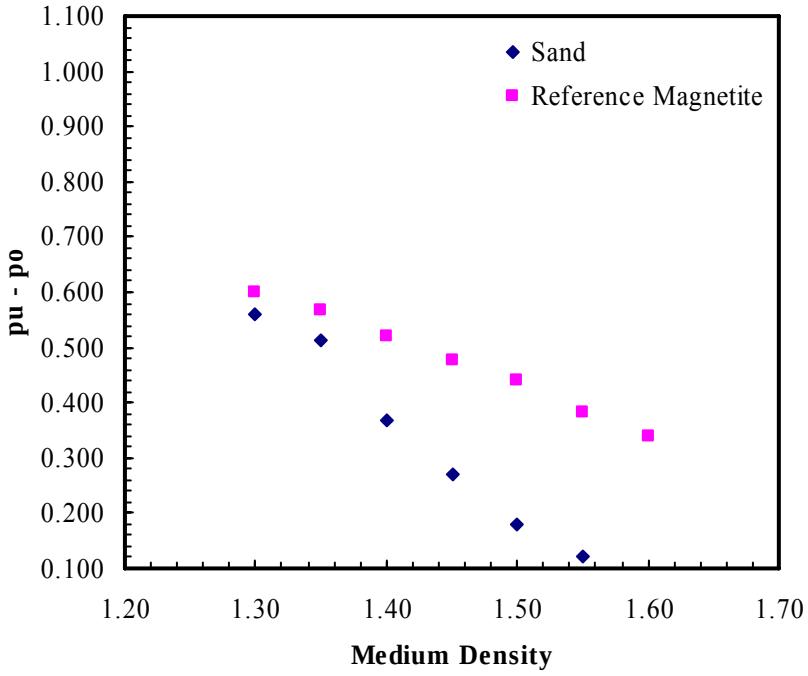

Figure 3. Suspension stability comparison between sand and reference magnetite at an inlet pressure of 5.0 psi.

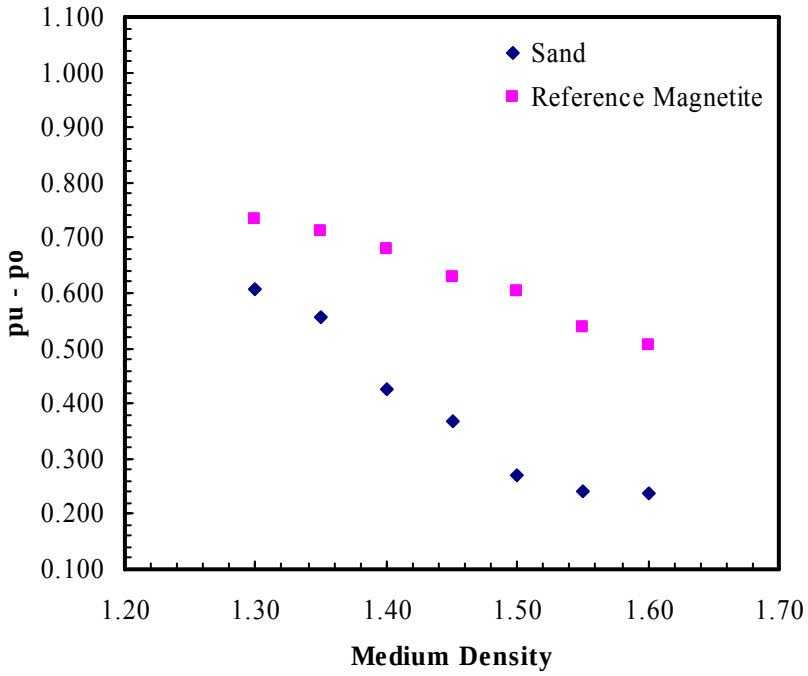

Figure 4. Suspension stability comparison between sand and reference magnetite at an inlet pressure of 7.5 psi.

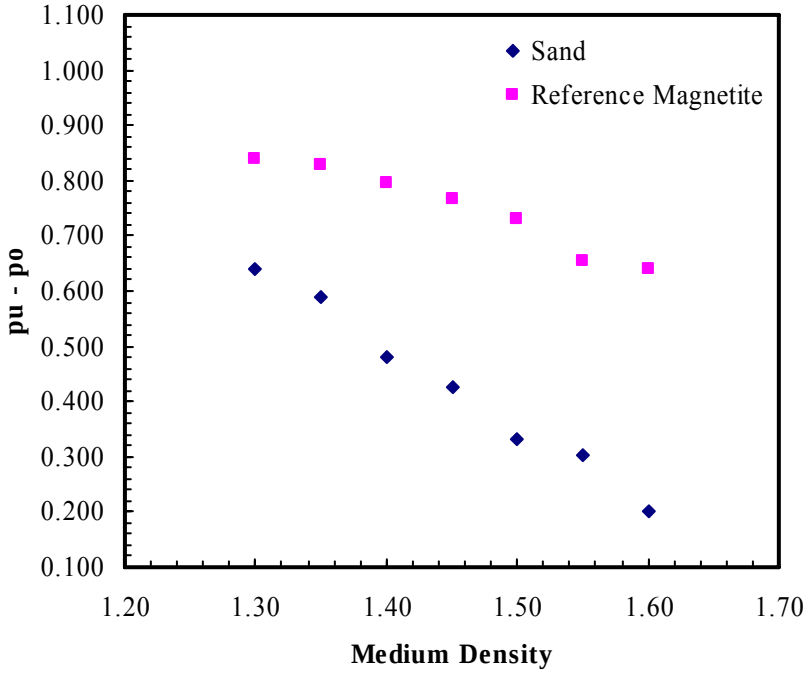

Figure 5. Suspension stability comparison between sand and reference magnetite at an inlet pressure of 10 psi.

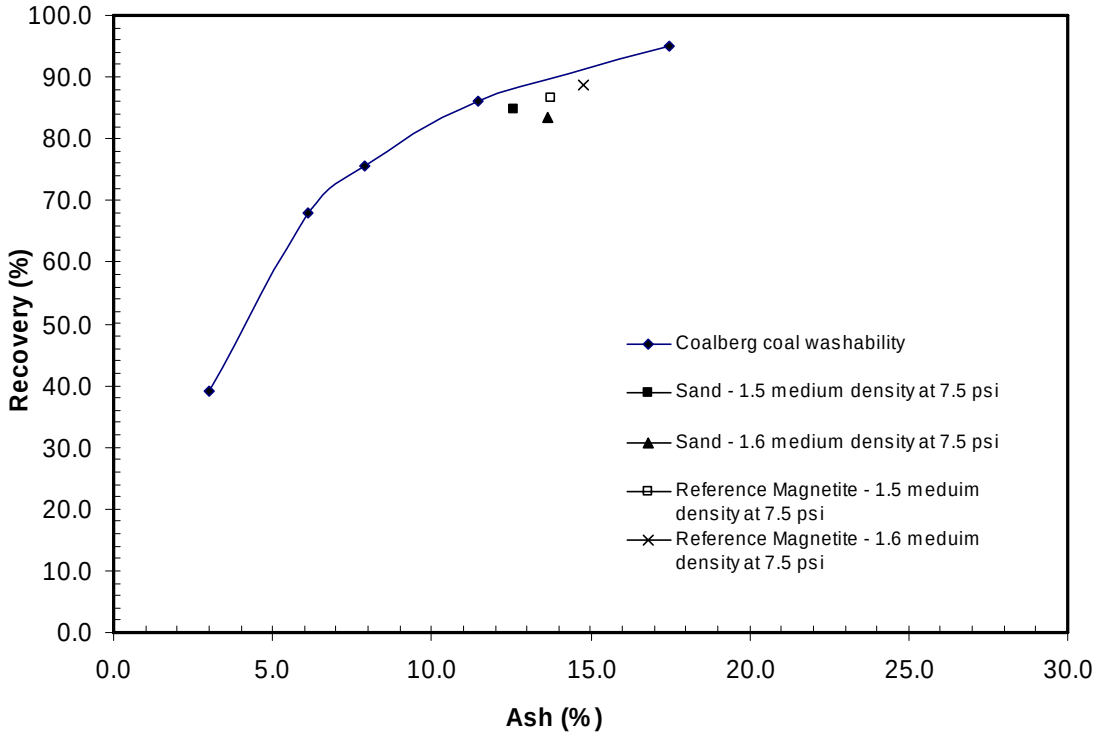

Figure 6. Comparison of actual dense medium cyclone performance with the Coalberg coal for the Reference magnetite in terms of product ash (%) vs. yield (%).

Table 3. Dense medium cyclone performances with 100 mesh sand and Reference magnetite at 7.5 psi.

Response Parameter	- 100 mesh sand		Reference Magnetite	
Medium Density (RD)	1.50	1.60	1.50	1.60
Feed Ash (%)	33.85	35.29	33.85	34.55
Product Ash (%)	12.59	13.66	13.76	14.77
Tailings Ash (%)	71.92	71.29	73.67	77.00
Yield (%)	64.17	62.48	66.47	68.21
Recovery (%)	84.79	83.35	86.65	88.83
Organic Efficiency (%)	97.68	93.65	97.25	97.62
d_{50}	1.620	1.680	1.624	1.742
E_P	0.059	0.064	0.037	0.035
$d_{50} - d_{medium}$	0.120	0.080	0.124	0.142
$d_{m\ underflow} - d_{m\ overflow}$	0.271	0.238	0.604	0.505

SUMMARY AND CONCLUSIONS

During this reporting period, fine sand was used to obtain a preliminary assessment of the ability to use plant fine waste material to form an adequate dense medium in coal cleaning applications. The separation performances achieved when cleaning ¼-in x 28 mesh Coalberg coal were compared with those obtained using commercial grade B magnetite. The investigation was performed using a 15-cm (6-in) diameter dense medium cyclone in a closed-loop circuit. The findings can be summarized as follows:

1. The stability of the sand suspension was significantly better than that provided by the reference magnetite of a broad range of medium densities and feed inlet pressures.
2. As expected, medium stability substantially improved with an increase in medium density and a decrease in feed inlet pressure. Stability is a function of particle population which determines the degree of hindered settling and the total system particle surface area which ultimately affects medium viscosity.
3. In general, the density offsets were lower with the sand-based medium as opposed to the reference magnetite suspension, which is likely due to better medium stability.
4. At a 1.5 RD, the sand-based medium provided an excellent separation performance as indicated by an organic efficiency of nearly 98%.
5. Viscosity effects apparently hampered separation performance at a 1.6 RD as indicated by a drop in recovery with an increase in product ash content. The organic efficiency decreased to about 94%.
6. The probable error values obtained for the sand-based medium were approximately 60% higher than those achieved using the reference magnetite.

As a result of the positive separation performances, flotation column tailings will be recovered from an operating preparation plant and tested as a magnetite alternative during the next reporting period.

Activities in the following areas were also realized during the current reporting period:

1. Steel slag samples were obtained from Stein, Inc who specializes in steel scrap processing. The steel slag for crushed to -100 mesh using a cage mill. The material will be evaluated in the dense medium circuit.
2. Another steel production waste material known as ‘C’ waste will also be evaluated. Reportedly, ‘C’ waste contains more iron and, thus, should be more magnetic. The quantity of ‘C’ steel waste in the U.S. is in the millions of tons.
3. Work is on-going to recover magnetic material from combustion fly ash using a spiral and magnetic separator.

FUTURE WORK

1. Evaluate the separation performance efficiency data generated from the use of the flotation reject.
2. Complete the evaluation of the coarse magnetite material for high-density separations.
3. Initiate work on the evaluation of the steel production waste sources.
4. Analyze the rheological properties of the various mediums.

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Appendix 12: Measurement of Surface Forces Between Hydrophobic Surfaces (VA016)

TECHNICAL PROGRESS REPORT

Contract Title and Number:	Period of Performance:
Crosscutting Technology Development at the Center for Advanced Separation Technologies (DE-FC26-02NT41607)	Starting Date: 6/1/2005 Ending Date: 10/31/2006

Sub-Recipient Project Title:	Report Information:
Measurement of Surface Forces Between Hydrophobic Surfaces	Type: Semi-Annual Number: 2 Period: 4/1/06-10/1/06
Principal Investigators:	Date:
Yoon	Code: VA016-R02
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Subcontractor Address:	Subcontractor Information:
Insert address of subcontractor. If none awarded, insert "No subcontracts issued."	Phone: Fax: E-Mail:

ABSTRACT

Froth flotation is the most widely used method for separating fine particles in the mining industry. The process is based on rendering a selected mineral hydrophobic, so that it can be separated from other minerals that are hydrophilic. Thus, control of particle hydrophobicity is critically important in flotation. However, the nature of the hydrophobicity is not fully understood, particularly in view of the forces acting between two hydrophobic particles suspended in water. In the current reporting period, surface force measurements have been conducted using an atomic force microscope (AFM). The force measurements were conducted with gold surfaces after coating them with xanthate surfactant. In addition, the adsorption process of xanthate ions onto gold was investigated by cyclic voltammetry (CV) and contact angle measurements, which show that the amyl xanthate can reversely adsorb on gold surfaces. Long range attractive forces in excess of van der Waals force have been detected using AFM for gold in amyl xanthate solution.

INTRODUCTION

Background

Froth flotation is the most widely used solid-solid separation technique in the mining industry. It is based on the hydrophobicity difference of particles. Thus, rendering an

interested mineral more hydrophobic than others is the key to the success of a flotation process. For this reason, the early days of flotation research was focused on hydrophobizing minerals and monitoring the changes in hydrophobicity by measuring contact angles. However, contact angle is a thermodynamic property and does not provide kinetic information. On the other hand, flotation is a kinetic process and the industry strives for improving flotation kinetics and, hence, increasing recovery and throughput.

In colloid chemistry, the kinetics of coagulation can be predicted by the DLVO theory, which considers two surface forces, namely, repulsive double-layer force and attractive van der Waals force. The theory is useful for describing interactions between particles. However, it is inadequate for studying bubble-particle interactions, as both of these forces are repulsive under typical flotation conditions. It was not until recently that one could actually measure the surface forces acting between two hydrophobic surfaces, and observed additional attractive force, which is naturally referred to as "hydrophobic force". It has been shown that the use of the hydrophobic force allows one to model coagulation of hydrophobic particles (Xu and Yoon, 1989, 1990) and bubble-particle adhesion (Yoon, 1991; Yoon and Mao, 1996; Mao and Yoon, 1997). However, there has been a great deal of controversy regarding the existence of the hydrophobic force and its possible origins. Furthermore, most of the hydrophobic force measurements conducted in the past was made with mica and silica surfaces using surfactants that are not commonly used for flotation. It is therefore, proposed to conduct direct force measurements using sulfide minerals, gold, and rutile (TiO_2) in the presence of thiols, cationic surfactants, and anionic surfactants. The results of the proposed work should help alleviate the controversy and collect information that can help further the flotation technology.

Objective and Approach

The objective in the reporting period is to perform direct measurement of forces acting between gold surfaces in xanthate solutions. Cyclic Voltammetry and contact angle measurements will be employed to investigate the adsorption process of amyl xanthate on gold. The obtained data is helpful for the controlling the hydrophobicity of gold in xanthate solution. The surface force measurement between gold surfaces in the amyl xanthate solutions will be conducted using AFM technique.

PROJECT TASKS

Task 1 Purification of Xanthates

Potassium amyl xanthate (KAX) was used in the experiment to hydrophobizing gold surfaces. The purification of xanthates was conducted by using pure acetone and diethyl ether, which is described in the literature (Rao, 1971). The xanthates were recrystallized at least twice prior to use.

Task 2 Electrochemical Measurements

Cyclic voltammetry (CV) was used to verify the chemisorption of the potassium amyl xanthate on gold surfaces. CV experiments were conducted in a standard electrochemical cell using a 273A potentiostat. The cell was equipped with a saturated calomel electrode (SCE) as reference electrode and a counter electrode made of platinum. Gold coated glass slide was used as working electrode, and 10^{-1} M of $NaClO_4$ was employed as supporting electrolyte. When testing the blocking capability of the xanthate layer, the electrolyte solution containing 10^{-2} M $K_3Fe(CN)_6/K_4Fe(CN)_6$ was used.

Cyclic voltammograms of gold electrode in 10^{-1} M $NaClO_4$ and 10^{-1} M+10^{-4} M KAX are shown in Fig. 1. The dotted curve represents the relationship of current density *vs.* potential for gold electrode in 10^{-1} M $NaClO_4$ electrolyte solution, while the cyclic voltammogram of gold in 10^{-1} M $NaClO_4$+10^{-4} M KAX is represented by the solid curve. For the dotted curve, during the anodic scan, the small anodic current at potential around 190 mV is supposed to be caused by the adsorption of perchloride ions on gold. And the anodic current at potential about 500 mV is believed to be due to the oxidation of gold. As the potential is swept in the reverse direction (cathodic scan), the reduction of gold begins at a potential about 150 mV. For the solid curve, the anodic current peak at -700 mV is attributed to the adsorption of xanthate ions, and the current peak at 250 mV is due to the oxidation of ethyl xanthate ions to diamyldixanthogen. The two cathodic current peaks around potential of -690 mV and -840 mV are believed to due to the reduction of diamyldixanthogen to amyl xanthate ions, and the desorption of amyl xanthate ions, respectively. The cyclic voltammetry experiment shows that the amyl xanthate ions from water solution spontaneously chemically adsorb onto gold surface and form xanthate layer.

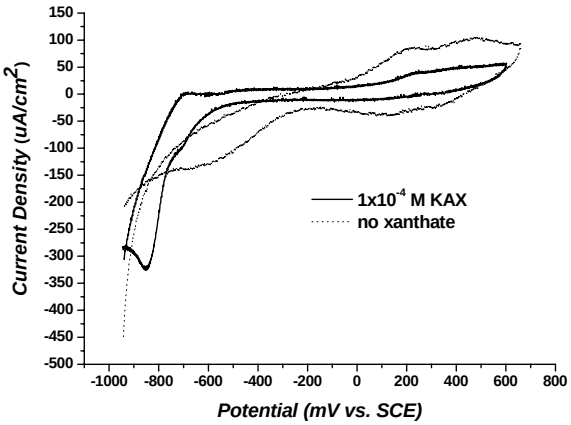

Fig 1. Cyclic voltammograms of gold in 10^{-1} M $NaClO_4$ solution with a scan rate of 250 mV/s.

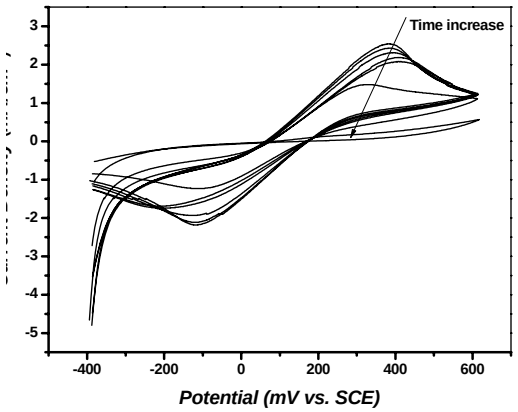

Fig 2. Cyclic voltammograms of gold recorded in 10^{-2} M $K_3Fe(CN)_6/K_4Fe(CN)_6$, 10^{-1} M $NaClO_4$ and 10^{-5} M KAX at different adsorption time, with scan rate of 200 mV/s.

The blocking capability of the xanthate layer formed with different immersion time towards the ferri/ferro redox couples was studied by cyclic voltammetry as shown Fig. 2. Application of a bare cleaned gold electrode gave the expected CV of $K_3Fe(CN)_6/K_4Fe(CN)_6$. It clearly appears that the blocking capability of xanthate layer to the access of the redox

couple to the Au electrode surface increases with time. After 1260 min of immersion time, the xanthate layer gave the highest efficient blocking capability, which indicates that the layers have few pinholes and defects. The layer is thus, from an electrochemical point of view, well packed. It is also indirectly indicates that the adsorption of amyl xanthate onto gold surface is a rather slow process, which requires at least 20 hours.

Task 3 Contact Angles Measurements

Contact angle measurement is another way to examine the adsorption process of amyl xanthate ions in water adsorb onto gold surface. The result of water contact angle of gold is shown in Fig 3. Generally, the contact angles of gold surfaces reach maximum value with less time for higher concentration of amyl xanthate, which means that the adsorption rate is determined by the concentration of xanthate in the bulk solution. In the xanthate solutions of higher concentrations (5×10^{-6} M, 1×10^{-5} M), the contact angles of gold decrease after reaching the maximum values. It is supposed that a second layer which reversely orients toward water bulk solution is formed. According to the above CV test, for the concentration of 1×10^{-5} M, the blocking capability reaches the highest level after an immersion time of 21 hours. While the contact angle measurement shows that the contact angle value of gold reaches maximum after 1 hour of immersion time in 1×10^{-5} M xanthate solution. It is suggested that the high contact angle might not determine the closely packed structure of the xanthate layer.

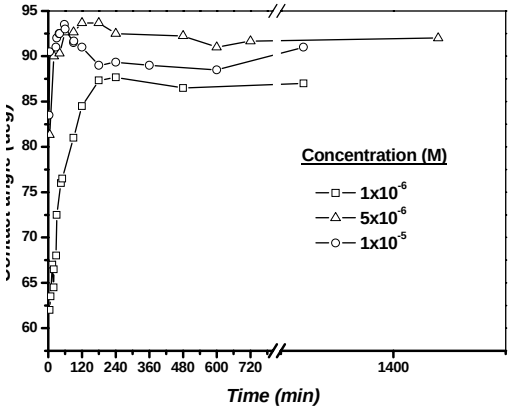

Fig 3. Contact angles of amyl xanthate layers on gold surface formed in different xanthate aqueous solutions with varying immersion time.

Task 4 Surface Force Measurements

Gold microspheres and gold coated glass flat plates were used in the surface force experiments during this reporting period. The surface forces were measured at room temperature (~25°C) using the colloidal probe technique developed by Ducker et al. (1991, 1992). Triangular cantilevers with spring constant of 0.58 N/m were used in the current experiment. To remove contamination, the gold coated glass plates were boiled in a H_2SO_4/H_2O_2 (Piranha solution) solution for 30 min, rinsed thoroughly with nanopure water and absolute ethanol. Figures 4, 5 and 6 show the results of measurement of the forces between a gold micro particle and a flat gold coated glass plate in aqueous KAX solution with different concentration (1×10^{-6} M, 5×10^{-6} M and 1×10^{-5} M) at varying immersion time. The experimental data show that the most attractive forces are much greater in magnitude than the van der Waals force. In the 1×10^{-6} M KAX solution, the repulsive force decreases with time, and the contact angle (from 81° to 87°) increases with time. In the 5×10^{-6} M KAX,

with the extending time, first the repulsive force decreases, and then becomes strongly attractive, then becomes repulsive again. For the contact angle, it increases at first (from 81° to 94°), and reaches maximum, then decreases (from 94° to 92°). In a higher concentration of 1×10^{-5} M, the strongly attractive force decreases with time. According to the above surface force data, it is confirmed that in the higher concentration of KAX solution, a second layer reversely adsorbs onto the first monolayer of KAX. The anionic group of KAX on the surface renders the repulsive double layer force, which counteracts the hydrophobic attractive force.

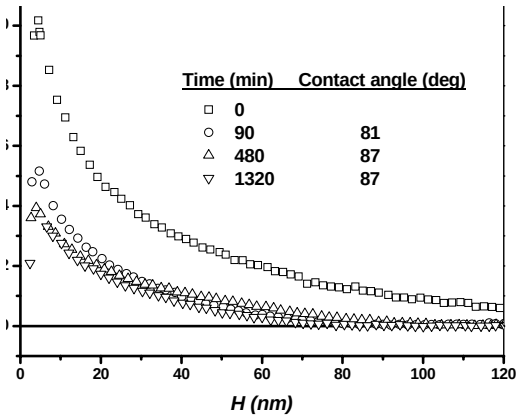

Fig 4. Surface forces in 1×10^{-6} M KAX aqueous solution.

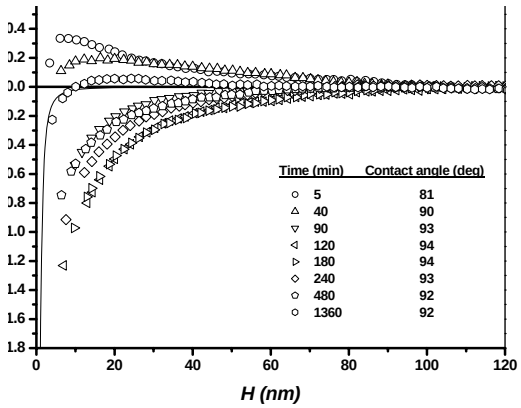

Fig 5. Surface forces in 5×10^{-6} M KAX aqueous solution.

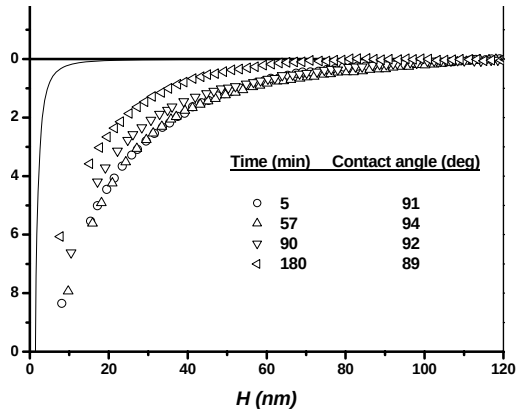

Fig 6. Surface Forces in 1×10^{-5} M KAX aqueous solution.

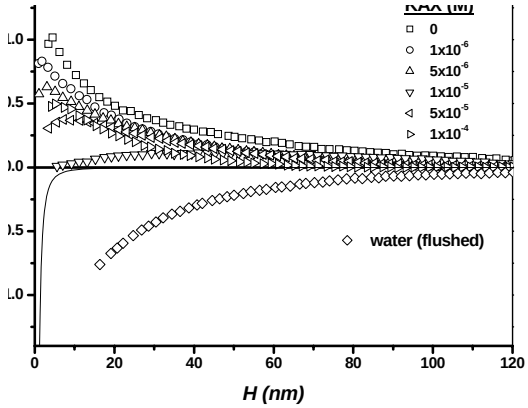

Fig 7. The surface forces as a function of concentration of KAX.

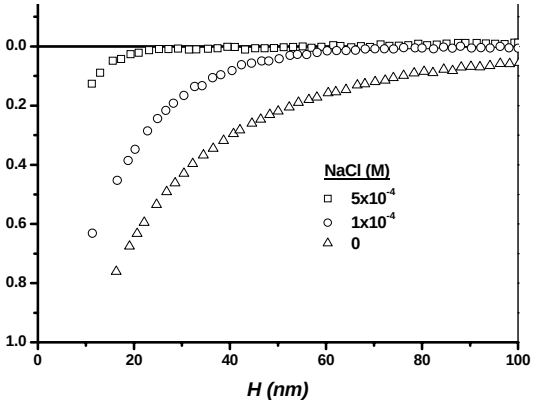

Fig 8. The surface forces between KAX hydrophobic layers in different concentration of NaCl aqueous solution.

To further explore the reverse orientation phenomena of KAX on gold, the surface force was measured as a function of concentration of KAX. The Fig 7 shows that, when the concentration of KAX surfactant is increased, first the repulsive force decreases, then becomes attractive, then becomes repulsive again. After adding the KAX solution with concentration of 1×10^{-4} M, the liquid cell was flushed with pure water. A strongly attractive hydrophobic force is observed. It is probably that the physically adsorbed top layer was removed by the flushing water.

After flushed with pure water, the liquid cell was filled by NaCl solution with different concentration (5×10^{-4} M and 1×10^{-4} M), and the experimental data is shown in Fig 8. It is shown that the addition of NaCl decreases the magnitude and range of the attractive hydrophobic force. It is believed that the addition of NaCl disturbs the water structure between the hydrophobic surfaces.

SUMMARY

During the current reporting period, CV, contact angle and surface force measurements were used to study the adsorption of amyl xanthate on gold, and the hydrophobic force between hydrophobic xanthate layer surfaces. The CV test verified the chemiadsorption of amyl xanthate on gold. The contact angle and surface force measurements revealed the reverse orientation phenomena of amyl xanthate on gold surface. According to the surface force measurement, the attractive hydrophobic force which is much greater in magnitude and range than expected for the van der waals force between hydrocarbon surfaces has been detected at the high water contact angles.

FUTURE WORK

Much of the work conducted during the next reporting period will focus on the surface force measurements between the ZnS surfaces.

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PUBLICATIONS/PRESENTATIONS

To date, no major publications have resulted from the current reporting period.

Appendix 13: Development and Testing of a Horizontal Pressure Belt Filter (VA010)

PROGRESS REPORT

Contract Title and Number:	Period of Performance:	
Crosscutting Technology Development at the Center for Advanced Separation Technologies (DE-FC26-02NT41607)	Starting Date:	10/1/2002
	Ending Date:	10/31/2006

Sub-Recipient Project Title:
Development and Testing of a Horizontal Pressure Belt Filter

Principal Investigators:
Gerald H. Luttrell and Roe-Hoan Yoon

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Subcontractor Address:
No subcontracts issued.

Report Information:
Type: Semi-Annual
Number: 6
Period: 10/1/05-3/31/06
Date: 4/30/06
Code: VA010

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ABSTRACT

A variety of mechanical processes are available for dewatering fine particles in the coal and mineral processing industries. Unfortunately, many of these processes suffer from major shortcomings such as poor dewatering performance, low throughput capacity, and high capital and operating costs. This project seeks to overcome these problems by developing a new type of dewatering process that combines the operational flexibility of a continuous belt filter with the dewatering efficiency of a batch pressure filter. The proposed project involves the design, construction, testing, and evaluation of a prototype unit and pilot-scale test circuit having a production capacity of approximately 100 lb/hr. Test data obtained from the project will be used to promote the engineering development of a full-scale commercial unit. During the past reporting period, most of the work conducted under this project has focused on the continued construction and shakedown testing of the prototype test unit.

INTRODUCTION

Background

Filtration processes are commonly used in the coal and minerals processing industry to remove excess moisture from the surfaces of fine particles. However, in order to overcome difficulties associated with the poor performance, extensive maintenance requirements, and high capital/operating costs of existing filter designs, a tremendous incentive exists to develop a filtration system. Ideally, the new filtration system needs to (i) make use of a high differential pressure, (ii) operate in a continuous mode, (iii) minimize filter cloth blinding while avoiding blow back of moisture, and (iv) offer operational flexibility in terms of independent control of cake thickness and drying cycle time. A process that is capable of meeting all of these criteria is a *horizontal belt pressure filter*. This new technology is very similar in design to that of a conventional horizontal belt vacuum filter, except the filtering mechanism is enclosed inside a pressurized chamber. During operation, feed is injected into the pressured chamber at the head of the filter belt. The high pressure drives the water through the filter cloth/belt where it is discharged into an effluent collection chamber maintained at atmospheric conditions. The filter cake is dropped into an air lock that sequentially opens and closes to continuously discharge the dried solids. Because of the high pressure differential, the filter cake produced by the new filter would be significantly drier than that obtained using disc or belt vacuum filters that are limited to a practical maximum differential pressure of approximately 0.8 atm. The elimination of the blow back of moisture during cake removal ensures that the driest possible cake is produced. Also, the capital cost of the compressor or staged blower can be less than 20% of the cost of a vacuum pump with an equivalent volumetric capacity. This difference would significantly reduce the cost of the proposed belt filtration system in comparison to vacuum based filters.

Objective and Approach

The primary objective of this project is to develop and test a *horizontal belt pressure filter* that is capable of efficiently dewatering fine coal in a cost effective manner. The new filter combines the operational benefits of a continuous belt filter with the dewatering efficiency of a batch pressure filter. The proposed project activities include project planning, equipment design/construction, shakedown testing, and detailed testing. In addition, a complete technical and economic evaluation of the new technology will be performed after the proposed experimental work has been completed.

PROJECT TASKS

Task 1 – Equipment Design/Construction

The mechanical construction of the prototype horizontal belt pressure filter was continued during this reporting period. Much of the work focused on the final assembly of the fabricated parts and the procurement of end caps for the pressure chamber. Figures 1 through 3 provide photographs of the key components of the assembled prototype.

Task 2 – Shakedown Testing and Modification

During the past reporting period, several series of shakedown runs were conducted at the Virginia Tech pilot-plant facility. The shakedown testing were necessary (i) to resolve deficiencies that were overlooked in the initial engineering design and construction of the prototype unit and (ii) to confirm that pumping capacities, pipe sizes, electrical supplies, control systems, etc., are adequate. Several technical issues that were resolved during this reporting period are discussed below.

- A new spring-loaded idler assembly was fabricated to control the tension in the filter cloth. This component was found to be necessary to ensure proper tension, alignment and tracking of the filter cloth which rides on the carrier belt (see Figure 5).

- The disc-shaped end plates that allowed access through each end of the pressure vessel were found to be inadequate to withstand the pressure force generated by the unit. As a result, the entire pressure vessel was shipped to an off-site contractor where the Plexiglas end plates were replaced by thicker (1-inch) steel end plates (see Figure 5). For safety reasons, the vessel was also pressure tested at 120 PSI using water to ensure that the unit could function at the maximum expected pressure of 60 PSI.

- Preliminary shakedown testing indicated that the aperture of the original filter cloth may not be suitable for all of the different types of coal slurries to be examined in the proposed experimental test program. Therefore, a second type of filter cloth with a larger aperture was purchased for the prototype unit.

- The peristaltic feed pump used to feed coal slurry into the pressure vessel was found to be inadequate to achieve the desired production rate when operated under pressure. A ball-and-seat diaphragm pump was also found to be unsuitable for the same reasons. Therefore, a progressive cavity pump was procured and successfully placed into service for feeding the fine coal slurry into the pressure vessel.

- The preliminary shakedown tests indicated that the reciprocal valves used for the cake discharge system did not seal adequately. This problem made it impossible to increase the air pressure in the test unit to the target values. This issue was resolved by returning the originally purchased valves to the manufacturer and replacing them with sealed-seat valves.

- The shakedown tests indicated that the Teflon-strip sealing system under the carrier belt needed to be improved to reduce gas consumption. Several modifications are currently underway to minimize this problem. These modifications include the addition of multiple bands of plastic “weather” stripping underneath the longitudinal length of the carrier belt and the installation of flexible rubber seals under each end of the belt.

SUMMARY

During the latest project period, construction and assembly of the major components of the pressure belt filter where completed. The pressure vessel was shipped to a fabrication and welding shop to have two sight glasses installed, to check all of the welds for safety reasons, and to manufacture two end plates for the vessel. Also, the fabrication shop performed a hydrostatic test on the completed vessel and determined that vessel is structurally sound. All of the electrical and pressure vessel safety checks have been completed. Shakedown testing is now underway (i) to complete the performance testing all of the major components, (ii) to test their operational effectiveness of the unit, and (iii) to remedy any design weaknesses that may be identified..

FUTURE WORK

Work during the next reporting period will continue to include some fabrication and assembly activities as required based on the results obtained from the shakedown tests. This work will be followed by a detailed test program and economic evaluation. The detailed test program will include a study of key operating variables including feed flow rate, feed solids content, feed size distribution, filter belt speed, filter cloth mesh size, and applied pressure.

REFERENCES

1. “Advances in Solid-Liquid Separation,” (H. Muralidhara, Ed.), Distributed by the Royal Society of Chemistry, Burlington House, London, England, Battelle Press Publishing, Columbus, Richmond, England, 1986, 485 pp.

2. “SME Mineral Processing Handbook,” (N. Weiss, Ed.), American Institute of Mining, Metallurgical, and Petroleum Engineers, Inc., Kingsport Press Publishers, Kingsport, Tennessee, 1985, pp. 9-14 – 9-26.

PUBLICATIONS/PRESENTATIONS

No publications or presentations have been given during the current reporting period.

Figure 1. Photograph of the assembled prototype horizontal belt pressure filter.

Figure 2. Side view of the pressure vessel with the belt assembly removed.

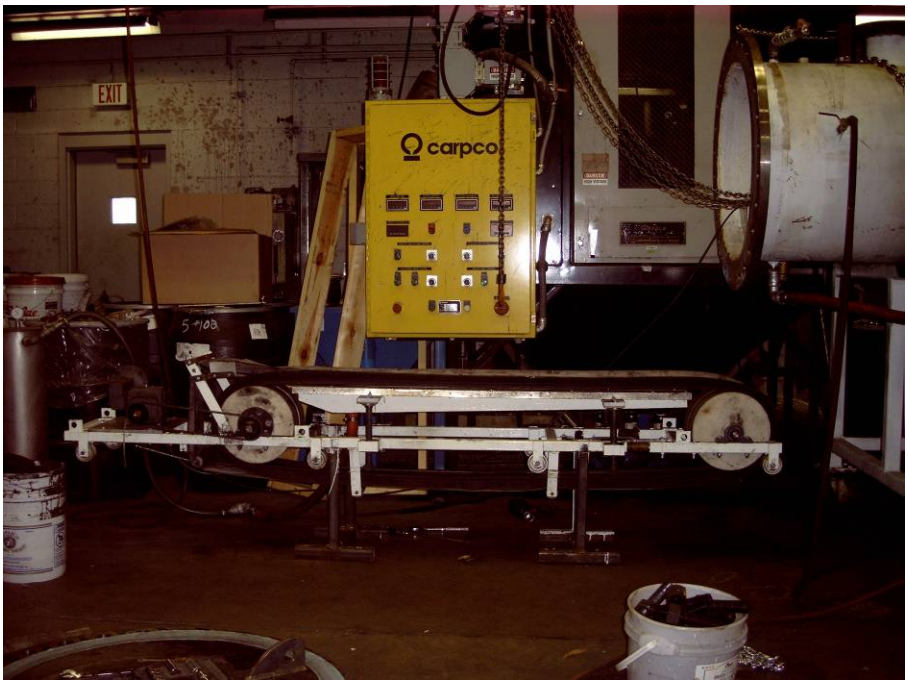

Figure 3. Side view of the horizontal belt filter assembly.

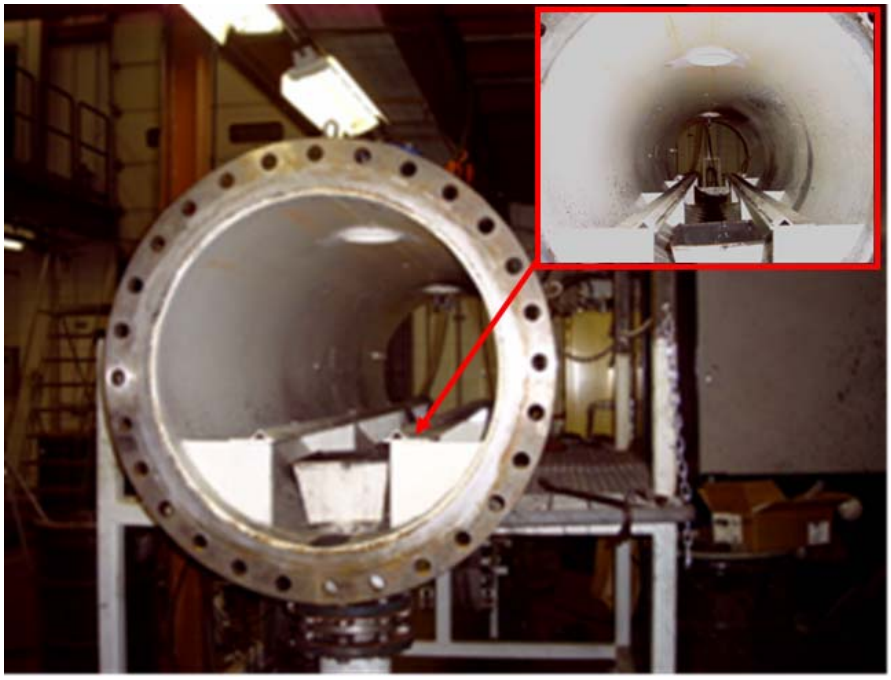

Figure 4. Track assembly inside the pressure vessel.

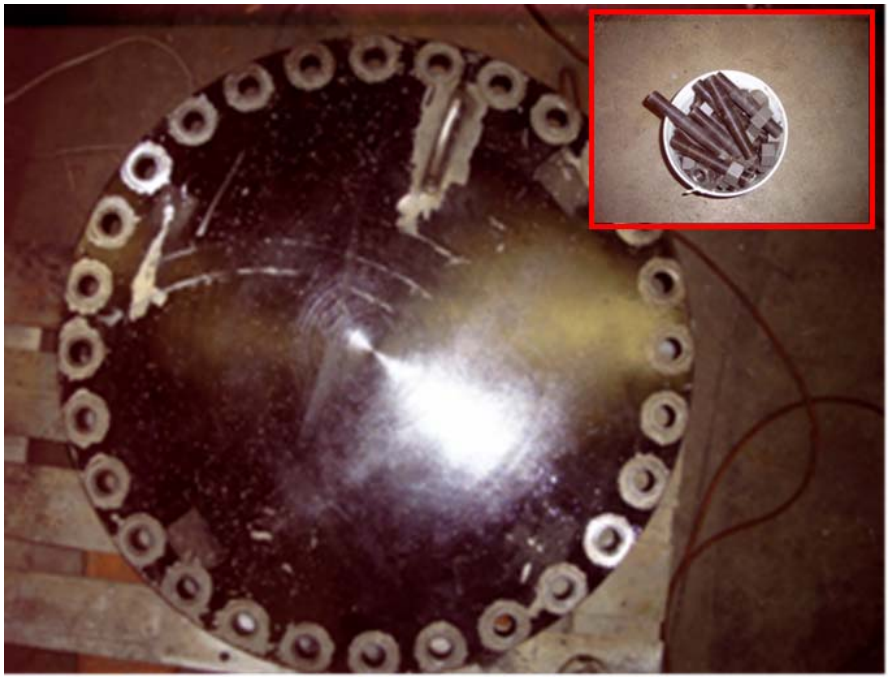

Figure 5. New end plate for the pressure vessel with 1-1/4 inch fastening bolts-nuts.

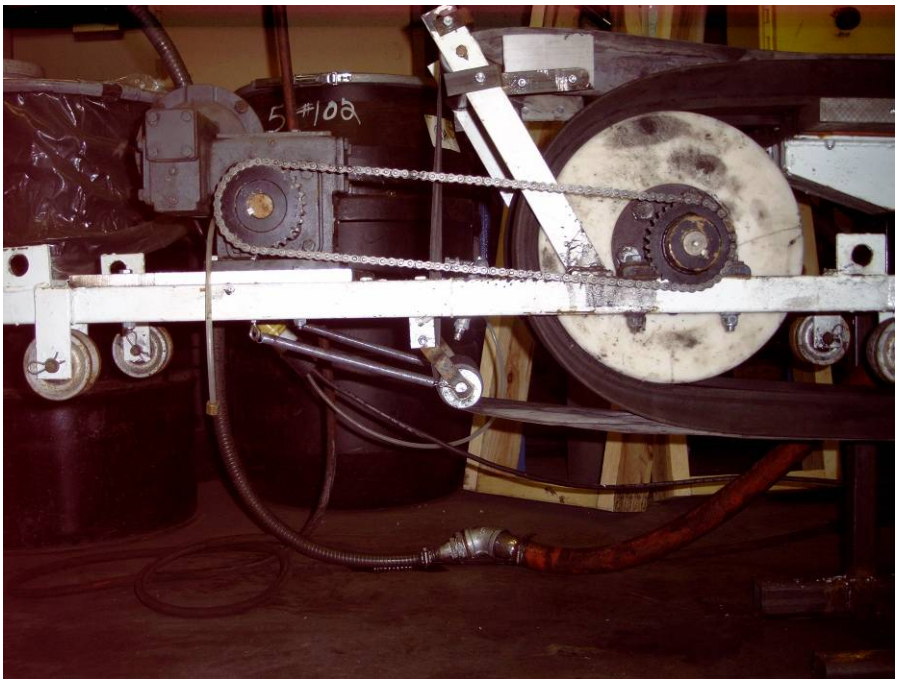

Figure 6. Spring tensioning idler used to tension the filter cloth belt.

Appendix 14: Development of a Fine Particle Centrifuge (VA006)

PROGRESS REPORT

Contract Title and Number:	Period of Performance:
Crosscutting Technology Development at the Center for Advanced Separation Technologies (DE-FC26-02NT41607)	Starting Date: 6/1/04 Ending Date: 10/31/06

Sub-Recipient Project Title:	Report Information:
Development of a Fine Particle Centrifuge	Type: Semi-Annual Number: 4 Period: 10/1/05-3/31/06
Principal Investigators:	Date: 4/30/06
Roe-Hoan Yoon and Gerald H. Luttrell	Code: VA006
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No subcontracts issued.	Phone: Fax: E-Mail:

ABSTRACT

The solid-solid separation processes employed by modern coal preparation plants require large amounts of process water. After cleaning, the unwanted water must be removed from the surfaces of the particles using mechanical dewatering equipment. Unfortunately, the processes used to dewater fine particles are inherently inefficient and costly to operate and maintain. To overcome this problem, a novel hyperbaric centrifugal filter has been developed by researchers at Virginia Tech. Preliminary test data obtained using a batch unit suggest that this new technology can reduce the moisture content of fine coal products by approximately 30-50% as compared to existing dewatering processes. The objective of this project is to construct a continuous prototype unit and to conduct a detailed experimental study of this new technology. During the current reporting period, three sets of shakedown tests were performed in batch mode to identify and resolve any additional operating problems. The preliminary test data show that moisture reduction is significantly improved with the injection of air, particularly at higher rotation speeds. In addition, circuit modifications have been made to allow the unit to operate in continuous mode to improve the capture of fines. These mechanical modifications have been completed and the continuous tests are underway.

INTRODUCTION

Background

One of the most difficult and costly steps in coal preparation is the removal of moisture from the surfaces of fine coal particles. Although thermal dryers can effectively reduce moisture, these units require large capital expenditures and stringent air quality standards make it impossible to obtain new operating permits. As a result, coal producers resort to mechanical systems for fine coal dewatering. Unfortunately, the performance of mechanical dewatering equipment diminishes sharply for particles finer than 0.1 mm. The unacceptably high moisture content associated with this fraction forces the majority of coal producers to discard their coal fines to waste impoundments. In the U.S. alone, approximately 2 billion tons of fine coal has been discarded in abandoned ponds and 500 to 800 million tons in active ponds. On a yearly basis, U.S. coal producers discard approximately 30 to 40 million tons of fresh coal fines into ponds. This represents a loss of valuable natural resources, loss of profit for coal producers, and creation of significant environmental concerns.

Objective and Approach

The availability of a low-cost mechanical dewatering device that can efficiently remove moisture from fine coal will greatly benefit the U.S. coal industry. In light of this need, researchers at Virginia Tech have developed a novel hyperbaric filter centrifuge that can reduce the moisture contents of fine coal by 30-50% as compared to currently available dewatering methods (Yoon and Asmatulu, 2000). The new technology employs both gas pressure and centrifugal force to increase the driving force for removing water from the fine capillaries present in a filter cake. The specific objectives of this project are (i) to construct a small-scale continuous prototype unit for testing, (ii) to evaluate the effects of key operating and design variables, and (iii) to demonstrate the capabilities of the new technology using fine coals from different coal preparation plants.

PROJECT TASKS

Task 1 – Filter Centrifuge Design/Construction

Most of the work done during this reporting period focused on the construction of the new drum seal and the fabrication of the parts needed to run the unit in continuous mode. The problem which allowed water to drip inadvertently into the cake collection chute was eliminated by the new seal design. The design of the feeding mechanism was also upgraded to allow the unit to run as a continuous unit. The batch unit mainly consisted of a pressurized rotating filter basket and a feed tank which is kept mixed all the time. The loss of ultrafine coal particles through the screen section of the rotating drum was the biggest issue with the batch unit. Preliminary tests indicated that up to 50% of the solids were reporting to the effluent for some fine feed coal samples.

To overcome the loss of fines, a thickener has been installed as a feed tank when the unit is operated in continuous mode. In this configuration, the thickener underflow is fed to the centrifuge while the effluent is fed back to the thickener (see Figure 1). This layout makes it possible to control cake moisture using the centrifuge and to control solids recovery using the thickener. Since maintaining a constant bed level in the thickener is critical for having a stable process, a fresh feed must be fed to the thickener when the bed level drops below a

certain predefined point. Another well mixed feed tank is used to supply fresh coal to the thickener tank. An electronic optical system has been installed and is being evaluated to automatically control the bed level in the thickener feed tank.

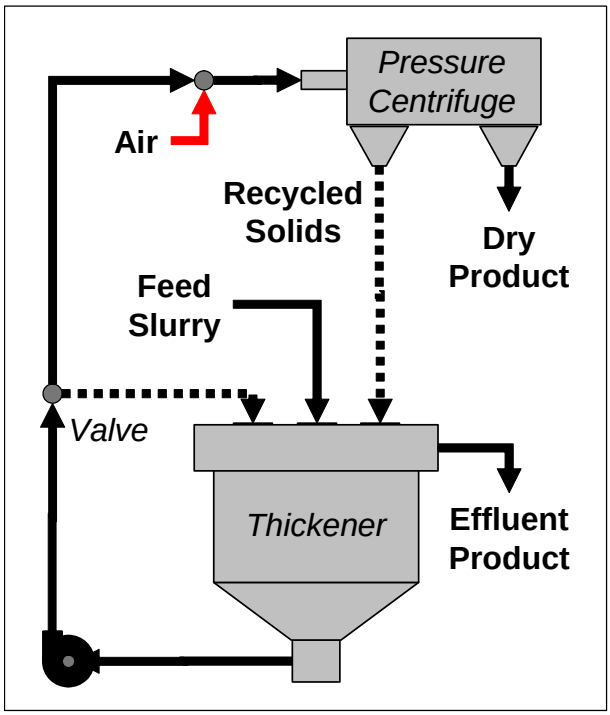

Figure 1. Hyperbaric filter centrifuge circuit.

Task 2 – Filter Centrifuge Testing

During this period of reporting, several series of shakedown tests were conducted in batch mode with the newly fabricated drum seal. The coal samples used in these tests were obtained from screen-bowl centrifuge feeds at existing coal preparation plants. The first set of tests were conducted at a constant fill time of 15 sec and air injection times of 0 (no air), 15 and 120 sec. The rotation speed was held constant at 1,100 rpm. A baseline moisture content of 15.6% was obtained when no air was injected. This value was reduced to 10.3% by injecting air for 15 sec and further reduced to 6.7% after 120 sec of pressurized air injection.

Based on these promising results from the initial shakedown tests, a second set of test runs were conducted using a fresh coal sample from the same industrial plant site. The tests were conducted using a 15 sec fill time and air injection times of 5, 10, 30, 60 and 120 sec. Three sets of tests were performed at rotation speeds of 1000, 1250 and 1500 rpm. The test results, which are summarized in Table 1, show that the moisture dropped from just over 20% at the lowest air injection time and rotation speed to below 11% at the largest air injection time and rotation speed. The data are plotted in Figure 1 for comparison. This plot shows that an increase in air injection time from 5 to 120 sec incrementally improved the moisture removal by about 5 percentage points for the lowest rotation speed of 1000 rpm. The incremental improvement was somewhat (i.e., about 3 percentage points) for the higher rotation speeds of 1250 and 1500 rpm. Unfortunately, a baseline test (with no air injection) was not run due to plugging of the feed line that occurred when no air was introduced.

One problem with the previous set of tests is that the total time of centrifugation increased as the air injection time increased. Therefore, it was not possible to distinguish whether the reduction in moisture observed in Figure 1 was due to a longer period or air injection or a longer period of centrifugation. To overcome this problem, a third set of shakedown tests was conducted in which the machine was rotated for the same total duration with and without the addition of air. A freshly acquired coal sample from the same preparation plant site was again used in these experiments. The test runs were conducted at the highest rotation speed (1500 rpm – 390 g's) centrifugation times of 5, 10, 30, 60 and 120 sec. The tests were repeated with and without injecting air for each of centrifugation time. In addition, the feed time was increased from 15 to 30 sec in this particular series of tests to increase the amount of solids retained within the unit. The results of these tests are summarized in Table 2. A comparison of the data is also provided in Figure 2.

Table 1. Batch test results obtained using the hyperbaric filter centrifuge (15 sec fill time).

Air Time (sec)	Rotation Speed (rpm)	Rotation Force (g's)	Moisture Content (%)	Cake Weight (gms)
5	1000	142	20.1	16.5
10	1000	142	20.2	18.51
30	1000	142	14.7	22.79
60	1000	142	18.3	31.5
120	1000	142	15.0	33.95
5	1250	222	13.3	7.18
10	1250	222	14.5	14.43
30	1250	222	14.2	18.31
60	1250	222	13.9	20.71
120	1250	222	13.9	25.62
5	1500	319	13.3	14.89
10	1500	319	13.9	12.66
30	1500	319	13.3	15.09
60	1500	319	13.2	14.69
120	1500	319	10.9	17.87

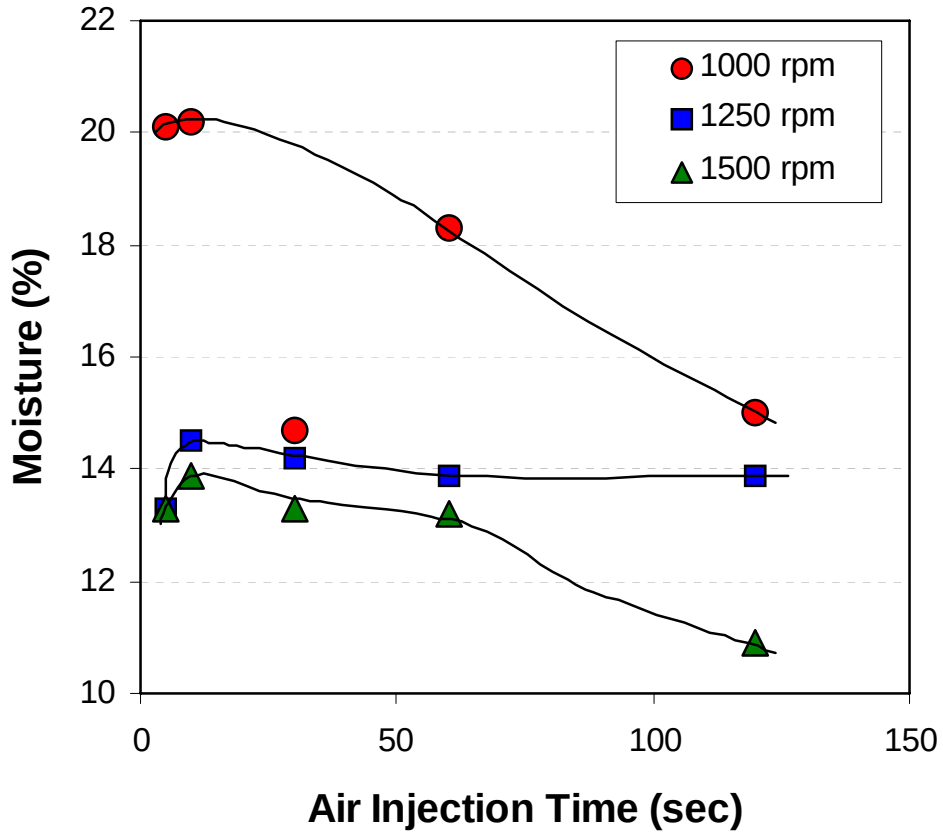

Figure 1. Batch test results obtained using the hyperbaric filter centrifuge (15 sec fill time).

Table 2. Batch test results obtained using the hyperbaric filter centrifuge (30 sec fill time, 1500 rpm rotation speed – 390 g's).

Air Injection Used?	Rotation Time (sec)	Moisture Content (%)	Cake Weight (gms)
No	5	12.6	77.15
No	10	11.2	94.37
No	30	10.8	95.73
No	60	10.2	104.6
No	120	9.6	96.89
Yes	5	10.6	116.62
Yes	10	10.3	86.91
Yes	30	9.6	130.96
Yes	60	8.3	72.4
Yes	120	9.7	109.83

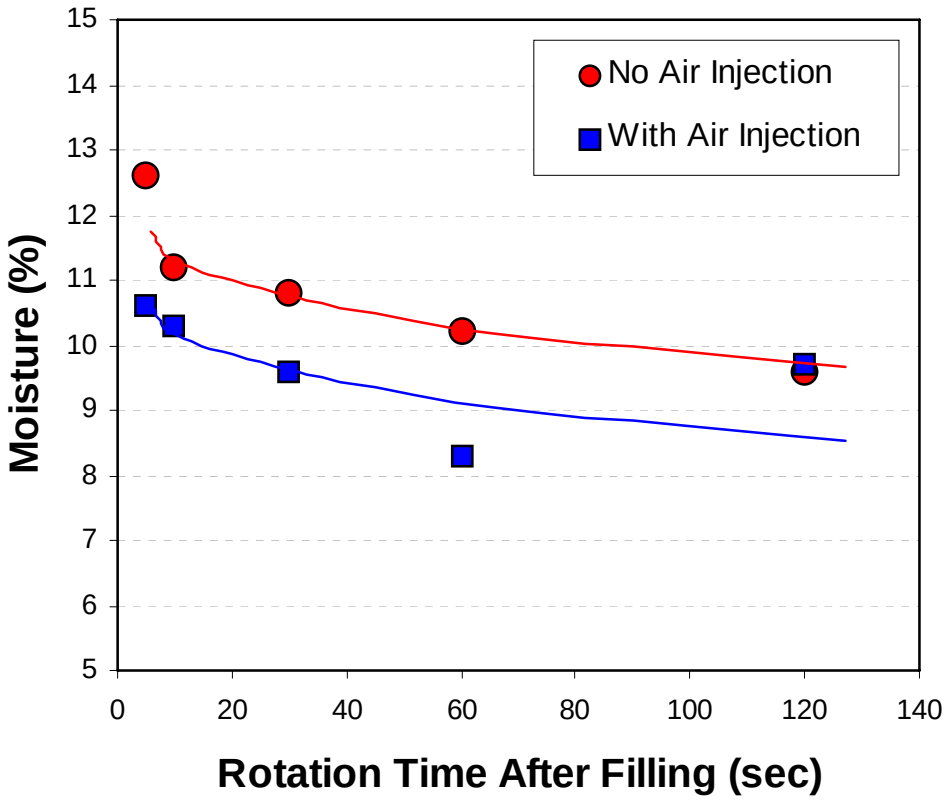

Figure 2. Batch test results obtained using the hyperbaric filter centrifuge (30 sec fill time, 1500 rpm rotation speed – 390 g's).

The test data indicate that the injection of air provided an incremental reduction in moisture removal of only about 1 percentage point. However, all of the moisture values obtained in this series of tests is already very low (around 12% total moisture or less). In fact, the values obtained with air injection at centrifugation drying times of 30 sec or greater are all single-digit values. These results suggest that either (i) the coal sample used in these tests contains very little fines or (ii) a large amount of the fines were lost through the screen section in the batch tests. Previous laboratory tests indicate that the differences in moisture obtained with and without air injection are much greater for cakes containing larger amounts of fine particles. Therefore, a much larger difference in moisture is expected once the continuous circuitry (i.e., integrated thickener) is operating and a proper circulating load of fines is maintained within the prototype. Continuous mode tests will be performed using the prototype during the next reporting period in order to verify this hypothesis.

Task 3 – Engineering Design

To date, no projective activities have been carried out under this particular task pending the completion of the construction and testing of the prototype unit.

SUMMARY

During this reporting period, construction of a continuous unit was continued and the problem in the mechanical water seal was eliminated. Several series of shakedown tests were carried out in batch mode. The data indicate that the moisture reduction is significantly better at higher rotation speeds and with the injection of air. However, the capabilities of the prototype cannot be fully established until additional tests are completed with the unit operating in continuous mode. This mode of operation required the integration of a thickening unit into the test circuitry. This modification makes it possible to improve fines recovery by circulating fines previously lost through the screen back to the circuit feed.

FUTURE WORK

Future work will involve any improvements necessary to achieve a stable process. Once proven, detailed tests will be run to fully evaluate the capabilities of the unit for a variety of coal samples and over a wide range of operating conditions.

REFERENCES

Yoon, R.-H. and R. Asmatulu, “Methods of Improving Centrifugal Filtration,” U.S. Patent Application Serial No. 09/531,373, filed March 21, 2000.

Yoon R.-H. and R. Asmatulu, PCT Patent Application Serial No. PCT/US02/11318, filed April 12, 2002.

PUBLICATIONS/PRESENTATIONS

To date, no major publications have resulted from this project.

Appendix 15: Improvements in Screen-Bowl Centrifuge Performance (VA013)

TECHNICAL PROGRESS REPORT

Contract Title and Number:	Period of Performance:
Establishment of the Center for Advanced Separation Technologies (DE-FC26-01NT41091)	Starting Date: 6/1/04 Ending Date: 10/31/06

Sub-Recipient Project Title:	Report Information:
Improvements in Screen-Bowl Centrifuge Performance	Type: Semi-Annual Number: 3 Period: 10/1/05-3/31/06
Principal Investigators:	Date: 4/30/06
Gerald H. Luttrell and Roe-Hoan Yoon	Code: VA013
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Subcontractor Address:	Subcontractor Information:
No subcontracts issued.	Phone: Fax: E-Mail:

ABSTRACT

Screen-bowl centrifuges are the most commonly used method for dewatering fine coal in the United States. Unfortunately, this process is the least efficient and most costly dewatering operation in the preparation plant. In light of these difficulties, a broad-based research project has been undertaken to develop technological enhancements that improve moisture reduction and increase fine coal recovery for screen-bowl centrifuges. The first part of this work involves a detailed in-plant test program to experimentally define the baseline operating capabilities of screen-bowl centrifuges. This fundamental information is needed so that plant operators can optimize the performance of their existing dewatering circuits. The second part of this work will involve the testing of internal injection ports for (i) adding flocculant to the low-solids pool and (ii) adding dewatering aids and surface tension modifiers to the dewater screen solids. During the past reporting period, several series of field tests were performed to further assess the performance of the flocculant injection system at an additional industrial plant site. These tests showed that the flocculant type and dosage is very important in maintaining low effluent solids. Work was also performed to complete the collection and analysis of samples needed to characterize the in-plant performance a a full-scale industrial screen-bowl centrifuge. Unfortunately, the test results obtained to date were inconclusive due to the large degree of scatter in the experimental test data.

INTRODUCTION

Background

The solid-solid separation processes employed by modern coal preparation plants require large amounts of process water. After cleaning, the unwanted water must be removed from the surfaces of the particles using mechanical dewatering equipment. Coarse particles can be readily dewatered using simple screening systems, while finer particles require more complicated unit operations such as centrifuges and filters for effective dewatering. In select cases, thermal drying may even be required to remove additional moisture so that the final product can meet customer specifications. Moisture that is not removed by these processes reduces the heating value of the final coal product and increases the transportation costs for the solid fuel. In addition, excess moisture can create significant handling problems for both the coal producer and downstream consumers by plugging chutes, bins, rail cars, etc. The problem can be particularly severe during winter months because of freezing.

Most of the preparation plants in the U.S. use screen-bowl centrifuges to dewater their fine products. Despite this popularity, there is surprisingly little fundamental information available that can be used to optimize centrifuge performance. Most existing guidelines for centrifuge selection and operation are based on empirical relationships or rule-of-thumb recommendations. For example, product moisture is typically estimated from the percentage of minus 325 mesh material present in the feed slurry. This relationship was originally developed in the early 1970s (Orphanos, 1974) and is often applied incorrectly. The actual correlation was developed using the percentage of minus 325 mesh material in the dewatered product and not the percentage present in the feed slurry. As a result, product moistures are often higher in actual practice than predicted by this relationship. Likewise, coal recovery is generally estimated by assuming that all the material coarser than 325 mesh will be recovered along with 50% of the minus 325 mesh. Obviously, neither of these relationships accurately account for site-specific differences in other characteristics of the feed slurry (e.g., particle size distribution, coal wettability, feed solids content, etc.) or variations in machine design and operating variables (e.g., feed rate, weir settings, scroll speed differential, bowl volume, screen length, etc.).

Objective and Approach

An improved understanding of the operating characteristics and technical capabilities of screen-bowl centrifuges would make it possible for plant operators to improve the performance of their dewatering circuits. Therefore, the objectives of this project are (i) to formulate detailed engineering criteria for optimizing the performance of industrial screen-bowl centrifuges and (ii) to develop and evaluate technological enhancements in screen-bowl centrifuge design that will improve moisture reduction and/or increase fine coal recovery.

PROJECT TASKS

Task 1 - Field Evaluation

This task involves the detailed evaluation of an industrial screen-bowl centrifuge at an industrial preparation plant site. The ultimate objectives of this work are (i) to derive engineering expressions that can be used to predict the moisture content and solids recovery attainable as a function of the various operating and design variables and (ii) to provide data that can be used to calculate the incremental moisture of the material that is discharged as the operation of the centrifuge is adjusted. During this reporting period, a mass-balance routine was developed to analyze the test data obtained from samples collected around an industrial-scale screen-bowl centrifuge. A typical set of size-by-size performance data is provided in Table 1. The individual groups of samples generally mass balanced well and, as such, were believed to be reliable. However, comparison of the results from tests conducted under different conditions indicated that there was considerable random variation in the samples (i.e., no clear trend could be observed between solids content or moisture as a function of feed flow rate or percent solids). As indicated in the last technical report, the large variation is believed to be due to large fluctuations in plant conditions created by variations in coal types, size distributions, etc. A second test site which is subject to less variability is currently is being sought for conducting a second round of in-plant tests.

Table 1. Typical set of size-by-size mass balance data for a screen-bowl centrifuge.

	Experimental Data				Balanced Data			
	Feed	Product	Drain	Effulent	Feed	Product	Drain	Effulent
Total Mass (% stream):								
Plus 100 M	63.62	**69.81**	**53.48**	**0.16**	63.33	70.38	53.31	0.16
100 x 325 M	13.82	**14.71**	**23.69**	**0.05**	12.99	14.44	24.04	0.05
325 M x 0	22.57	**15.48**	**22.83**	**99.78**	23.68	15.18	22.65	99.79
Overall	100.01	100.00	100.00	99.99	100.00	100.00	100.00	100.00
Total Mass (tph):								
Plus 100 M	63.62	62.92	3.21	0.02	63.33	63.31	7.78	0.02
100 x 325 M	13.82	13.26	1.42	0.00	12.99	12.99	3.51	0.01
325 M x 0	22.57	13.95	1.37	9.84	23.68	13.65	3.31	10.03
Overall	**100.00**	90.13	6.00	9.87	100.00	89.95	14.60	10.05
Ash (% stream):								
Plus 100 M	4.44	**5.87**	**5.35**	**59.84**	5.01	5.00	5.30	59.82
100 x 325 M	10.97	**7.48**	**15.40**	**26.11**	8.08	8.07	16.03	26.11
325 M x 0	16.65	**12.71**	**19.69**	**23.85**	17.13	12.53	19.59	23.39
Overall	8.09	7.17	11.00	23.91	8.28	6.58	11.12	23.45
Total Ash (tph):								
Plus 100 M	282.24	369.36	17.17	0.94	317.23	316.26	41.26	0.96
100 x 325 M	151.57	99.18	21.89	0.13	104.99	104.86	56.27	0.13
325 M x 0	375.61	177.34	26.97	234.79	405.76	171.10	64.79	234.66
Overall	809.34	645.87	66.03	235.88	827.97	592.22	162.31	235.75
Slurry Data:								
Solids (%)	24.51	**83.37**	**29.57**	**3.29**	24.18	83.36	29.57	3.29
Rate (tph)	407.99	108.11	20.29	299.88	413.49	107.90	49.36	305.59

Task 2 – Flocculant Addition

Several series of field tests were performed at an additional plant site to verify that the injection of polymer flocculant into the dilute pool section of a screen-bowl centrifuge would improve solids recovery. In this particular series of tests, a specially formulated polymer (SR polymer) prepared by Nalco chemical was compared with traditional cationic and anionic flocculants. The results obtained these in-plant tests are summarized in Table 1. In each experimental run, the as-received reagents (polymer or flocculant) were diluted with fresh water down to a 1% solution before being injected into the screen-bowl. The test data from the first series of tests (day 1) show that the solids content in the main effluent was reduced as the polymer dosage was increased up to 4.5 GPM. The highest dosage rate of 4.5 GPM reduced the solids content from about 3.9% to 0.6% (2.30 to 0.36 TPH). Poorer solids contents of about 2.7% were obtained at lower dosages of 1.25 and 2.50 GPM of polymer. In addition, test results obtained from a second series of tests (day 2) conducted at a fixed reagent dosage of 4.5 GPM showed that the polymer was superior to traditional anionic flocculant. The cationic flocculant also appeared to work well in the injection tube and reduced the solids content from 4.2% down to just over 1%. The moisture and ash contents of the dewatered products from these tests increased slightly when adding polymer due to the capture of ultrafine particles.

Table 1. Summary of screen-bowl centrifuge injection tests.

Test Description	Reagent Addition (GPM)	Dewatered Product			Effluent Discard		
		Ash (%)	Moist. (%)	Rate (TPH)	Ash (%)	Solids (%)	Rate (TPH)
No Reagent	--	8.70	12.84	25.72	9.58	3.94	2.30
SR Polymer	1.25	8.63	12.26	26.45	9.44	2.69	1.57
SR Polymer	2.50	8.48	15.77	26.47	8.61	2.66	1.55
SR Polymer	4.50	8.97	16.54	27.66	8.32	0.62	0.36
No Reagent	--	8.94	11.44	25.69	9.10	3.99	2.33
No Reagent		8.17	11.62	25.57	11.99	4.19	2.45
SR Polymer	4.50	9.23	16.96	27.41	9.74	1.84	1.07
Cationic Floc	4.50	8.65	15.31	25.93	10.07	1.05	0.61
Anionic Floc	4.50	8.74	11.66	25.36	9.68	3.58	2.09

Task 3 – Surfactant Addition

No additional experimental test work or analyses were performed under this task during this reporting period.

SUMMARY

Field tests conducted in the present work again demonstrate that flocculant injection can be used to effectively reduce the solids content of main effluent that is discarded by a screen-bowl centrifuge. The in-plant tests indicate that both reagent dosage and type is important in obtaining the best overall results. The test data also suggest that the moisture content of the screen-bowl product may increase slightly due to the recovery of fine particles displaced from the main effluent. For the tests conducted to date, the data suggest that the increase in moisture is only about 2 percentage points.

FUTURE WORK

During the next reporting period, test work will again focus on the characterization of full-scale screen-bowl centrifuge performance at an industrial site. The tests are to be performed as a function of key operating variables (i.e., feed slurry flow rate and solids content).

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PUBLICATIONS/PRESENTATIONS

R.T. Burchett, K.M. McGough and G.H. Luttrell, 2005. "Improved Screen-Bowl Centrifuge Recovery Using Polymer Injection Technology," 22*th* Annual International Coal Preparation Exhibition and Conference, Lexington, Kentucky, 10 pp.

G.H. Luttrell, R.T. Burchett, K. McGough and F. Stanley, 2006., "Improving Screen-Bowl Centrifuge Performance," SME Annual Meeting, St. Louis, Missouri, March 26-29, 2006, 5 pp.

Appendix 16: Ion Exchange Recovery of Cobalt from Copper Leach Solutions (NM002)

TECHNICAL PROGRESS REPORT

Contract Title and Number:	Period of Performance:
Establishment of the Center for Advanced Separation Technologies (DE-FC26-01NT41091)	Starting Date: 04/10/03 Ending Date: 05/30/05

Sub-Recipient Project Title: Ion Exchange Recovery of Cobalt From Copper Leach Solutions	Report Information: Type: Semi-Annual Number: 007 Period: 04/01/06-09/30/06
Principal Investigators: I. Gundiler and M.J. Hatch	Date: 09/06/06 Code: NM002-R07
Contact Address: New Mexico Tech Bureau of Geology & Min. Res. 801 Leroy Place Socorro, NM 87801	Contact Information: Phone: (505) 835-5730 Fax: (505) 835-6333 E-Mail: gundiler@gis.nmt.edu
Subcontractor Address: "No subcontracts issued."	Subcontractor Information: Phone: Fax: E-Mail:

ABSTRACT

Five new chelating ion exchange resins were synthesized and tested in small columns for absorption of cobalt, nickel and copper from acidic solutions. The resins were also tested with copper leaching raffinate solution obtained from a large copper mining operation in the Southwest. Of the new resins CHEL-38 (highly picolylated diethylenetriamine), CHEL-40 (less picolylated diethylenetriamine), and CHEL-73 picolylated diethylenetriamine showed the most promise. Commercially available bis-picolylamine and hydroxy propylpicolyl polyamine resins were also tested under the same conditions and compared with the newly synthesized resins. With appropriate raffinate feed volumes, the new CHEL-40 and CHEL-73 resins have a much higher absorption capacity for Co^{2+} in comparison with the commercially available resins. They also had as good or better capacity for Cu^{2+}, Ni^{2+} and Zn^{2+}. The CHEL-40 resin also had less capacity for Fe^{3+}, which is a highly desirable advantage for recovery of copper and cobalt from leach solutions. In acid elution, all the transition metal cations except Cu^{2+} were eluted easily from the CHEL-40 resin with water and 0.1M H_2SO_4 solutions. The absorbed Cu^{2+} required somewhat more concentrated H_2SO_4 for effective elution.

INTRODUCTION

Background

Cobalt is a strategic and critical metal which is used in production of mainly super alloys, and various other alloys and chemicals. It is not mined nor refined in the United States. The nation's needs are met with imported supplies and recycled alloys.

Leach solutions in large hydrometallurgical copper extraction operations in the Southwest generally contain 0.02-0.10 Kg/m^3 of cobalt. If cobalt can economically be recovered from the leach solutions, it could potentially supply a significant portion of the U.S. imports. Currently, the technology to recover the metal from these solutions economically is not available.

Ion exchange processes could recover cobalt present at low concentrations in copper raffinate solutions but commercially available resins are either too expensive, or may not function in acidic solutions. Chelating ion exchange resins may also be considered as potential substitutes for the organic liquid extractants used for copper extraction to eliminate fire hazards and potential for ground water pollution.

Objectives and Approach

This project was initiated to synthesize and test new chelating resins which could operate at low pH solutions and has higher capacity for copper and cobalt than available resin, and explore the possibility of recovering cobalt from the copper raffinate solutions.

PROJECT TASKS

Data Analysis and Discussion

No new experiments were conducted since the last reporting period. We had planned to do further studies to improve on the synthesis of particularly CHEL-40 and CHEL-73 resins, and synthesize larger batch of resins for bench scale testing during the summer semester. However, due to personnel issues, these plans did not materialize. We are currently in the process of preparing the final report and it should be submitted by the next reporting deadline.

SUMMARY AND CONCLUSIONS

Small particle size picolylated diethylenetriamine ion exchange resins tested in small columns at slow and moderately fast flow rates for absorption of cobalt and copper at very low concentrations (10, 16ppm Co^{2+}; 25, 40ppm Cu^{2+}) in a pH 2.1 copper raffinate solution showed that capacity for absorbing cobalt increased on CHEL-40 resin over that found in our earlier fast flow tests. However, the slow flow rates had little or no effect on the capacity for absorbing copper. Our newly synthesized picolylated

diethylenetriamine resin CHEL-73 (which was slightly less picolylated than the CHEL-40 resin) absorbed cobalt at moderately high flow rates as well as did a lesser volume of CHEL-40 at a slow flow rate.

Comparison tests were made with the commercially available hydroxypropyl picolylamine resin and dipicolylamine resin ground to similar particle sizes. Our new picolylated polyamine resin (CHEL-40) showed the best comparative capacity for cobalt, copper and nickel, and desirably, the least Fe^{3+} capacity in the column absorption tests at fast flow rates. Both our new resins performed better than the commercially available resins, especially for cobalt absorption capacity from the pH 2.1 mining raffinate. When 200 bed volumes of the raffinate solution was passed at high flow rates on a small bed of the best performing new resin (CHEL-40), significant amounts of cobalt and nickel were absorbed on the resin along with only a minor amounts of iron from the raffinate. The absorbed cobalt (along with nickel, iron and zinc) could be eluted easily from the resins by using water and 0.1M H_2SO_4. The absorbed copper required 1M H_2SO_4 solutions for effective elution.

Elution with 0.5- 2M H_2SO_4 of both the CHEL-40 and CHEL-73 resins which were loaded with appropriate volumes of raffinate feed yielded main eluate fractions whose cobalt concentration was over 10 times, and the copper concentration of over 50 times those present in the raffinate feed solutions.

Although these enrichment ratios are well within the conventional ion exchange separation guidelines, utilization of these resins ion the copper mining industry for the intended purpose is not very likely at this time due to low absorption capacity for cobalt and the high cost of picolylamine based resins. However, these resins could find ready applications in other industries, such as electro-plating and cobalt refining for purification of mother liquors from copper and nickel. Currently industrial partners are being sought for commercializing these resins and potential patent applications are being considered.

PUBLICATION

M.Sc Thesis, Premchandar Nandikhonda (Nov. 2005), “Preparation, Characterization, and Performance of Several New Chelating Resins for Recovery of Cobalt and Copper from Acidic Mining Solutions”, New Mexico Institute of Mining and Technology, Chemistry Dept Socorro, New Mexico, 87801 USA

ATTACHMENT

M.Sc Thesis, Premchandar Nandikhonda (Nov. 2005)

Appendix 17: Phyto-Extraction / Fabrication of Gold and Silver Nanoparticles (WV012)

TECHNICAL PROGRESS REPORT

Contract Title and Number:	Period of Performance:
Crosscutting Technology Development at the Center for Advanced Separation Technologies (DE-FC26-02NT41607)	Starting Date: 6/1/2004 Ending Date: 10/31/2007

Sub-Recipient Project Title:	Report Information:
Phyto-Extraction / Fabrication of Gold Nanoparticles – Feasibility Study	Type: Semi-Annual Number: 4 Period: 4/1/06-9/30/06 Date: 8/31/06 Code: WV012-R04
Principal Investigators: Ray Y. K. Yang, Eung Ha Cho	
Contact Address: Ray Y. K. Yang Chemical Engineering Department West Virginia University Morgantown WV 26506-6102	Contact Information: Phone: (304) 293 2111x2419 Fax: E-Mail: ryang@mail.wvu.edu
Subcontractor Address: No subcontracts issued	Subcontractor Information: Phone: Fax: E-Mail:

ABSTRACT

Gold nanoparticles were produced from the leaf extracts of three cultivars of geranium. The bio-formation process appears to be very rapid, achieving high concentrations of gold nanoparticles in about 35 to 60 minutes. The nanoparticles produced were found to remain stable for several months. The intra-cellular contents of gold in the cells of carrot, periwinkle, and stevia in suspension cultures and in the sprouts of mung bean and alfalfa are noticeably enhanced, overall, as the gold concentrations in contact with the plant cells or the sprouts increase, confirming the extraction and transportation of gold ions into the cells of the plants tested. In addition, the contents of gold in cells cultivated in suspension cultures are, in general, much more than several-fold higher compared to that in sprouts. This indicates the potential of using suspension culture of plant cells for large scale production of gold nanoparticles.

INTRODUCTION

Background

Phytomining is the production of a metal by growing high-biomass plants that hyper-accumulate high concentrations of a target metal. A conventional phytomining operation would consist of planting a hyperaccumlator crop over a low-grade ore body or mineralized soil, followed by harvesting and incineration of the biomass to ash to produce "bio-ore". In this project, we have expanded conventional phytomining to include other forms of plants, notably sprouts and plant cells.

Some plants are natural hyperaccumulators, while others require induction for hyperaccumulation. For most metals the threshold concentration for hyperaccumulation is 1 mg/g dry biomass, except for gold, which is 1 :g/g dry biomass [1-4]. Red beet (*Beta vulgaris*), carrot (*Daucus carota*), and mustard (*Brassica junces*) have been shown [2, 5] to be the plants with the best potential for phytomining for gold, if chemically induced by adding ammonium thiocyanate to the auriferous substrate to solubilize gold. The existence of gold nanoparticles in live alfalfa grown on agar-agar was observed using X-ray absorption spectroscopy and transmission electron microscopy by Gardea-Torresdey et al. [6].

Objective

Three separate tasks are conducted simultaneously in this project to determine the capability of whole plants and plant cells to extract and transport gold, as well as to show the existence of gold nanoparticles. The objective is to provide a better understanding of gold nanoparticles phyto-extracted and phyto-fabricated by hyperaccumulator plants, sprouts, and plant cells grown in suspension cultures, aiming eventually to develop feasible processes for large scale phyto-production of gold nanoparticles.

PROJECT TASKS

Task 1 – Investigation of gold nanoparticles in hyperaccumulator plants

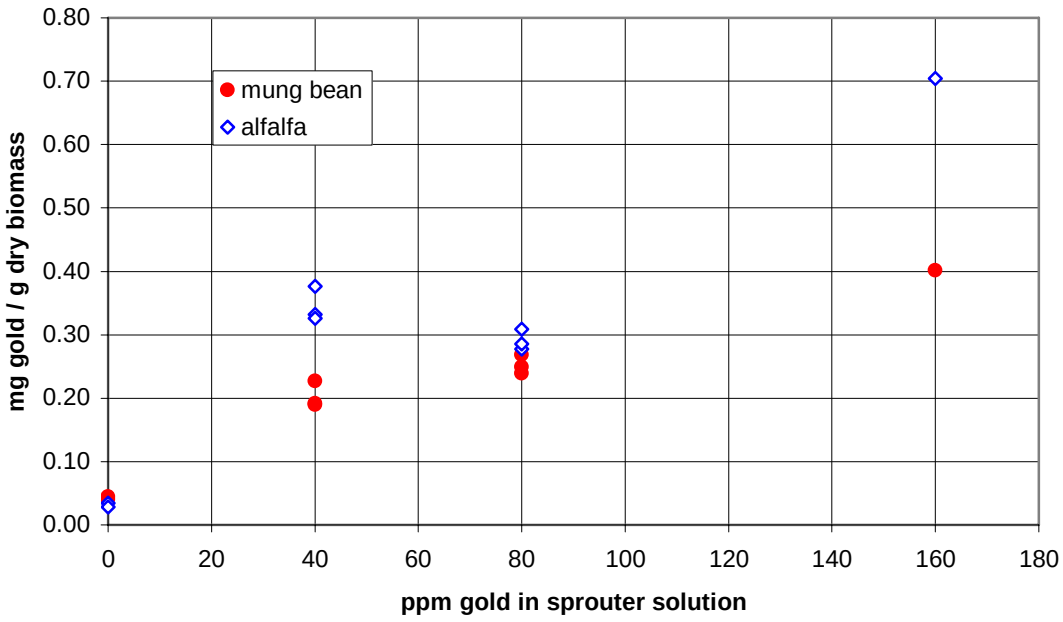
In the 10-week greenhouse experiment, 120 hyperaccumulator plants (in six cultivars with two cultivars of carrot, beet, and mustard) were grown in 120 pots (half of them in auriferous sand and the other half in pure sand), treated with ammonium thiocyanate 10 days before harvest, washed carefully to remove sands from all parts of plant (including root), air-dried on clean plastic surface for several weeks in greenhouse, and then stored in separate new paper bags. During this project period, the dry plant in each of the 120 bags was separately ground and any sands still attached to plant, particularly roots, were removed. The dry plant biomass of each sample was then burned at 700 ^{o}C to produce "bio-ore" (ash), which was then dissolved in *aqua regia* and analyzed by an atomic absorbance spectrophotometer (AAS). The data from this large-scale experiment have just been obtained and are currently being analyzed.

Task 2 – Investigation of gold nanoparticles in sprouts

As reported before, in this task mung bean (*Vigna radiate*) and alfalfa (*Medicago sativa*) were grown from seeds on two different types of sprouter, A and S, using potassium tetrachloroaurate solution of different concentrations. Difference in these two types of

sprouters, as well as the procedures for production of soot-free ash (bio-ore) from the sprouts and for determination of gold contained therein using an AAS, were described in Report: WV012-R2. Presented in Figures 2.1 below are the data collected for S-sprouter. As expected, the sprout data indicate that, overall, as the concentrations of gold in the potassium tetrachloroaurate solutions used in the sprouters increase from 0, 40, 80 to 160 ppm, the gold contents in the bio-ores also increase. In addition, overall, alfalfa sprouts appear to extract and retain higher concentrations of gold than mung bean sprouts. Not surprisingly the gold contents of sprouts grown in S-sprouter are much lower than that grown in A-sprouter, since the latter allows all part of the sprouts to be in contact with gold-containing sprouter solution.

Figure 2.1 Dependence of gold concentrations in mung bean and alfalfa sprouts on gold concentrations in sprouter solutions for type S sprouter

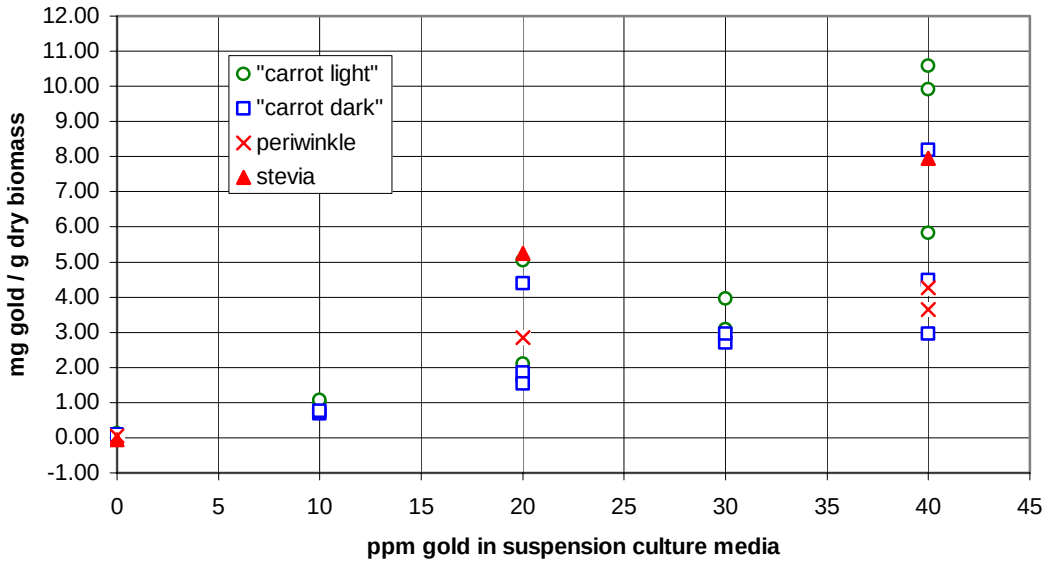


Task 3 – Investigation of gold nanoparticles in plant cells

During this reporting period, five callus cultures established before have continuously been maintained by subculturing every four weeks. These callus cultures include carrot (*Daucus carota*) and periwinkle (*Catharanthus roseus*) in Murashige and Skoog (MS) solid medium, red beet (*Beta vulgaris*) on solid agar Gamborg's B5 medium, and stevia (*Stevia rebaudiana*). For carrot, two types of culture have been maintained since its initiation; one that has been kept in the dark all the time (designated as "corrot dark") and another in 12-hour light/dark (designated as "carrot light"). The suspension cultures of "carrot light", "carrot dark", periwinkle, beet, and stevia, which were successfully initiated and established from their corresponding callus cultures before, have been maintained in shakers located in three separate incubators with different light/dark patterns during this reporting period by subculturing every two weeks. The three light/dark patterns are: 12-hour light/dark (for periwinkle and "carrot light"), 24-hour light (for stevia), and 24-hour dark (for "carrot dark").

Shown in Figure 3.1 are the gold contents of cells of periwinkle, “carrot light” and “carrot dark” after exposing the cells to 20 ppm and 40 ppm of gold in the suspension cultures for one week. Similar to treatment for sprouts, the plant cells, after filtering out from their media, were washed repeatedly with distilled de-ioned (DD) water and then dried in an oven before burning in a muffle furnace to produce a soot-free ash, i.e., “bio-ore”. Each batch of bio-ore was dissolved in concentrated *aqua regia* and then analyzed for gold using an AAS.

Figure 3.1 Dependence of gold concentrations in carrot, periwinkle, and stevia cells on gold concentrations in suspension culture media



The data in Figure 3.1 indicate that, overall, intra-cellular contents of gold in all species of cells increase with increasing concentration of gold in the suspension medium. Similar trend was also observed in the case of silver nanoparticles. More importantly, as expected, comparing the data in Figures 3.1 with that in Figures 2.1(for S-sprouter) and Figure 1 in Report: WV012-R03 (for A-sprouter), one can observe that, though plant species are different, in general, the contents of gold in cells cultivated in suspension cultures are much more than several-fold higher compared to that in sprouts. This result indicates the potential of using suspension culture of plant cells for large scale production of gold nanoparticles.

A series of exploratory experiments were conducted with the ruptured leaves of three cultivars of scented geranium, “Rober’s Lemon Rose” (RR), “Rose”(R), and “Lady Plymouth” (LP), to investigate the factors affecting extra-cellular formation of gold nanoparticles in the broth of geranium leaves. Our major finding during this period is that exposure to either light or oxygen has no observable effects on the bio-formation of gold nanoparticles. The nanoparticle forming reaction is very rapid, as indicated by the very fast

increase in the intensity of the color of the broth with time soon after the addition of dilute potassium tetrachloroaurate solution, and the reaction appears to be completed in about 35 to 60 minutes, much shorter than that for silver nanoparticles. The final color of the mixture indicates extremely high concentration of gold nanoparticles produced.

Shown in Figure 3.2 are the colors of the final mixtures with 20 time dilution so the color differences between species, if any, may be detected. The three long vials shown in the picture on the left are the same vials shown in the photo on the right. In the latter, bottles having much larger diameters than the vials and containing exactly the same mixtures as in the corresponding vials are added to show the slight variations in colors due to different lengths of light paths.

Figure 3.2 Colors of aqueous solution of gold nanoparticles produced from three cultivars of geranium: "Rober's Rose" (RR), "Rose"(R), and "Lady Plymouth" (LP)

The colors of RR and R are quite close, both pink-ruby red, considered as the typical color of gold nanoparticles in aqueous medium [7], but the color of LP is light blue. Spectrophtometer measurements of the samples of 20X diluted final mixtures show that the gold surface plasmon resonance bands occur at approximately 525, 526, and 533 nm, respectively, for R, RR, and LP. These values are quite close to the range of 510-560 nm reported in the literature for an unknown cultivar of geranium [7]. However, unlike that of RR and R, our spectrophotometer measurement of LP shows a second peak at 642 nm, suggesting that gold nanoparticles formed with LP may be significantly anisotropic, leading to the distinctly different bluish color. On the other hand, gold nanoparticles formed with RR and R, having only one peak, may be predominantly more isotropic in shape. No observable changes in the colors of the samples of the 20X diluted final mixtures were detected even after several months of storage, indicating that the gold nanoparticles produced are very stable.

SUMMARY

Gold nanoparticles were produced from the leaf extracts of three cultivars of geranium. The bio-formation process appears to be very rapid, achieving high concentrations of gold nanoparticles in about 35 to 60 minutes. The nanoparticles produced were found to remain stable for several months. The intra-cellular contents of gold in the cells of carrot, periwinkle, and stevia in suspension cultures and in the sprouts of mung bean and alfalfa are noticeably enhanced, overall, as the gold concentrations in contact with the plant cells or the

sprouts increase, confirming the extraction and transportation of gold ions into the cells of the plants tested. In addition, the contents of gold in cells cultivated in suspension cultures are, in general, much more than several-fold higher compared to that in sprouts. This indicates the potential of using suspension culture of plant cells for large scale production of gold nanoparticles.

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Appendix 18: Recovery Of Gold From Thiosulfate Leach Liquor Using Activated Carbon (MT005)

TECHNICAL PROGRESS REPORT

Contract Title and Number:	Period of Performance:
Crosscutting Technology Development at the Center for Advanced Separation Technologies (DE-FC26-02NT41607)	Starting Date: 6/1/2005 Ending Date: 10/31/2007

Sub-Recipient Project Title:	Report Information:
Recovery Of Gold From Thiosulfate Leach Liquor Using Activated Carbon	Type: Semi-Annual Number: 2 Period: 4/1/06-9/31/06 Date: 8/28/06 Code: MT005-R02
Principal Investigators: Youmg, Twidwell	
Contact Address: Metallurgical and Materials Engineering Montana Tech Butte MT 59701	Contact Information: Phone: (406) 496-4158 Fax: (406) 496-4664 E-Mail: CYoung@mtech.edu
Subcontractor Address: No subcontracts issued.	Subcontractor Information: Phone: Fax: E-Mail:

ABSTRACT

This project was approved by CAST in mid-July of 2005 but official spending approval from Montana Tech was not received until November of 2005. A graduate student started working on the project in August of 2005 but, due to personal reasons, decided to leave campus in September at the start of the Fall 2005 Semester. His replacement was not found until April 2006. This report therefore contains data that was generated essentially in the month of August of 2005 by the first student and since May 2006 by the second student. In this study, a novel carbon adsorption technology for extracting gold from thiosulfate solutions is examined. Unless pretreated, activated carbons will not adsorb gold thiosulfate. However, by first adsorbing copper cyanide onto the carbon, gold thiosulfate can then be adsorbed in what appears to be an ion-exchange reaction. Copper cyanide was adsorbed at pH 10.5 and was found to yield higher adsorption densities than at pH 11. The difference is attributed to solution speciation. When the Cu-pretreated carbon was placed in gold thiosulfate solutions, gold take-up was observed with gold/copper ratios of 1:1 at pH 10.5 for all concentrations; however, at pH 11, ratios of 1:1 were observed only at low concentrations. Higher concentrations yielded a ratio of 0.6:1. Clearly, the results show that the envisioned process works but needs considerable more work to characterize as well as optimize.

INTRODUCTION

Background

In current commercial leaching of gold using cyanide (CN^-), gold (Au) in an ore is oxidized and dissolves to form the cyano-aurous complex ($Au(CN)_2^-$):

$$Au + 2\,CN^- \rightarrow Au(CN)_2^- + e^- \quad [1]$$

which requires oxygen (O_2) to be reduced to hydroxide (OH^-) in the presence of water (H_2O):

$$O_2 + 2\,H_2O + 4\,e^- \rightarrow 4\,OH^- \quad [2]$$

When electron-balanced, the overall reduction/oxidation (redox) reaction results:

$$Au + 2\,CN^- + ¼\,O_2 + ½\,H_2O \rightarrow Au(CN)_2^- + OH^- \quad [3]$$

The process was patented by MacArthur and the Forrest (1887) and was conclusively shown to be electrochemical in nature by Kudryk and Kellogg (1954) but was not generally combined with carbon adsorption technology until about 1970 (Marsden and House, 2006):

$$Au(CN)_2^- + C_{site} \rightarrow Au(CN)_{2\ ads}^- \quad [4]$$

This concentration step is dependent on the complex chemistry of the aurous species.

The standard reduction potential for oxygen to water is 1.23 V vs SHE, and the standard reduction potential for the non-complexed aurous ions is 1.69 V vs SHE, which means that, thermodynamically, free aurous ions are a stronger oxidizing agent than oxygen. However, in the presence of cyanide ions, the stability of the gold (I) cyanide complex lowers the standard reduction potential to -0.57 V vs SHE thus enabling the univalent ions to be processed under ambient conditions. In practical gold cyanidation, copper competes for cyanide ions with gold and leads to high cyanide consumption rates. Because the copper in the ore is present in significantly larger amounts than the gold, the resulting copper cyanide is also at significantly higher concentrations and thereby competes with gold cyanide for the adsorption sites on the activated carbon (Jay, 2000).

Gold leaching with thiosulfate is a leading contender to replace cyanide in the extraction of gold from ore. In several respects, the process is similar to cyanidation. This is envisioned by comparing Reactions 3 and 5 as well as by the standard reduction potential being lowered, in this case to 0.153 V vs SHE:

$$Au + 2\,S_2O_3^{2-} + ¼\,O_2 + ½\,H_2O \rightarrow Au(S_2O_3)_2^{3-} + OH^- \quad [5]$$

This makes the reaction amenable for use with air oxidation. Various chemicals are added to help stabilize the thiosulfate including copper which also helps to catalyze the leaching reaction (Marsden and House, 2006). However, a major limitation for the development of

thiosulfate leaching technology is the recovery of gold from leach liquors. Because activated carbon has a very low affinity for gold thiosulfate, it cannot be used like it is used with cyanide leach liquors:

$$Au(S_2O_3)_2^{3-} + C_{site} \rightarrow \text{No adsorption} \quad [6]$$

In this regard, extensive research efforts have turned to developing resins and other technologies for gold recovery. However, resins suffer from fouling and, of course, are inherently expensive. An anti-fouling and cheaper alternative is therefore needed to make the technology competitive against cyanidation.

Objective and Approach

The main objective of this project is to develop a recovery technology for extracting gold thiosulfate from solution. It was therefore proposed (Young and Twidwell, 2005) that a non-resin technology be examined to assure that it works, does not suffer from the same limitations as resin, and will be compatible with existing gold cyanide production technology. An activated-carbon process was envisioned in which the carbon was pretreated with copper cyanide:

$$Cu(CN)_2^- + C_{site} \rightarrow Cu(CN)_2^-{}_{ads} \quad [7]$$

with the resulting pretreated carbon being used to extract the gold from thiosulfate solution:

$$Au(S_2O_3)_2^{3-} + Cu(CN)_2^-{}_{ads} \rightarrow Au(CN)_2^-{}_{ads} + Cu(S_2O_3)_2^{3-} \quad [8]$$

Assuming that the adsorbed cyano-aurous species produced by this "ion-exchange" method is the same as that produced by direct adsorption of the cyano-aurous complex (see Reaction 4), than current technology for carbon elution, electrowinning, and smelting can be used to produce gold bullion. To obtain these objectives, the approaches for the research are to (Task 1) verify that Reaction 8 occurs, (Task 2) determine parameters that critically affect Reaction 8, (Task 3) optimize Reaction 8 to maximize gold recovery from solution, (Task 4) spectroscopically and thermodynamically characterize the adsorbed species via comparison to direct adsorbed species, (Task 5) determine if conventional technology can be used to elute the adsorbed species, (Task 6) examine carbon nanotubes (CNT's) as a possible high-surface area adsorbent, (Task 7) develop a method for making CNT's from coal, and (Task 8) conduct a literature review throughout the project.

PROJECT TASKS

Current work is being done to optimize the copper cyanide adsorption onto activated carbon according to Reaction 7. The $Cu(CN)_2^-$ complex is desired for its ability to readily adsorb, more so than $Cu(CN)_3^{2-}$ or $Cu(CN)_4^{3-}$ (Marsden and House, 2006). This complex species is sensitive to CN:Cu mole ratio. A ratio of approximately 2-2.5 is needed for $Cu(CN)_2^-$ to be dominant in the solution (Jianming, 2002). Speciation is also affected by

temperature, initial copper concentration and to a lesser degree, pH. At these low ratios E_H-pH diagrams show the species to be stable in a range of pH from 6-12.

Potassium cyanocuprate (PCC) is used in the solutions needed for testing. Its dissolution rate in water is better than that of copper(I) cyanide, but requires testing to determine both copper and cyanide concentrations. Adjustments to pH are done at the time of dissolution and kept constant at 10.5. Activated carbon, obtained from Newmont Labs in Denver, Co., is added in predetermined increments. The solution is agitated for approximately one hour. Other process variables have not yet been utilized to determine optimum adsorption.

Carbon fines are removed from solution using a .45 micron syringe filter. The solution is then analyzed by ICP for determination of remaining copper concentration. Adsorbed copper is interpreted as:

$$[Cu+]_{adsorbed} = [Cu+]_{initial} - [Cu+]_{final} \quad [9]$$

Data collected since June is not included but shows a need for cyanide concentration testing of the PCC solution. No appreciable adsorption was seen and is likely caused by a CN:Cu ratio that is not suitable in this instance, but can be corrected by the additions of CuCN(s) or NaCN(s) as necessary. It may also be attributed to the new carbon being used which is being examined as well.

A final procedure for use with the PCC continues to be in development. At the point where the solution concentrations can be reproduced reliably and meaningful data can be obtained, the process variables will be manipulated to determine the working parameters for maximum adsorption. However, it is noted that the literature review is near completion except for ongoing library searches to keep updates as the project proceeds.

SUMMARY

A novel carbon adsorption technology for extracting gold from thiosulfate solutions was examined. Unless pretreated, activated carbons will not adsorb gold thiosulfate. However, by first adsorbing copper cyanide onto the carbon, gold thiosulfate was adsorbed in an ion-exchange reaction. Copper cyanide was adsorbed at pH 10.5 and was found to yield higher adsorption densities than at pH 11. The difference was attributed to solution speciation. When the Cu-pretreated carbon was placed in gold thiosulfate solutions, 100% gold extraction was observed as long as enough copper on the carbon was present. Gold-to-copper ratios of 1:1 were observed at pH 10.5 for all concentrations; however, at pH 11, ratios of 1:1 were observed only at low concentrations. Higher concentrations yielded a ratio of 0.6:1. Differences can also be attributed to solution speciation but may also have been caused by differences in researchers, experimental procedures, and activated carbons as discovered during this latest research campaign. Clearly, the envisioned process works but needs considerable work to characterize as well as optimize.

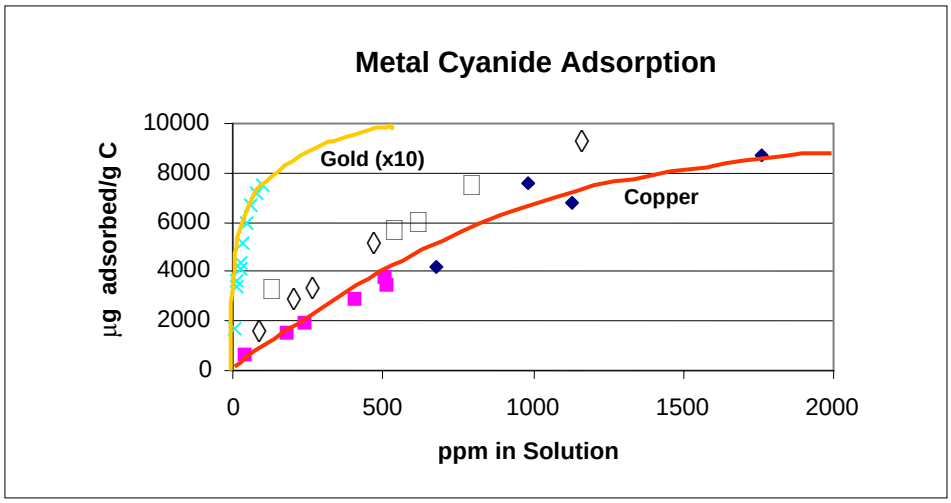

Figure 1. Adsorption isotherms on carbon for copper cyanide compared to literature for gold cyanide (Marsden and House, 2006). Closed symbols are preliminary data conducted at pH 11 for the proposal (Young and Twidwell, 2005) and open symbols are current data conducted at pH 10.5 for the project.

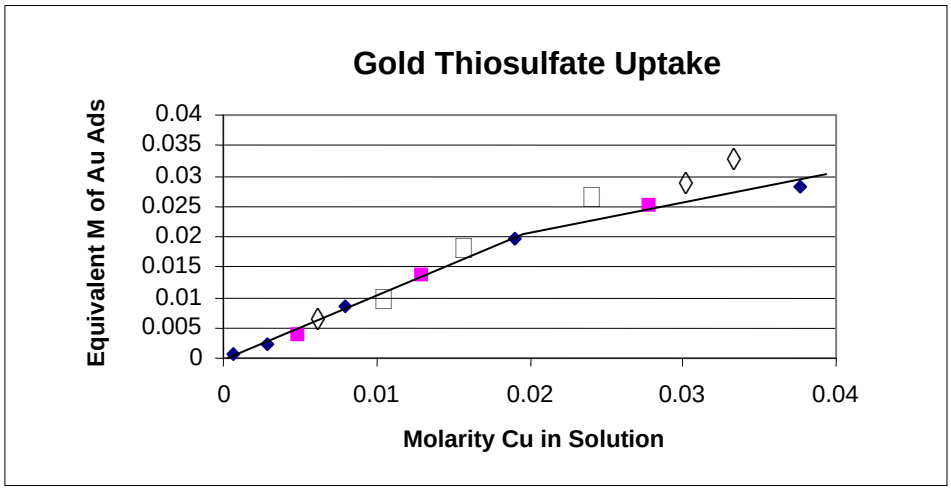

Figure 2. Gold uptake from thiosulfate solutions by copper-activated carbon as a function of copper displaced. Closed symbols are preliminary data conducted for the proposal (Young and Twidwell, 2005) using carbon pretreated with 4700 ppm Cu. Open symbols are current data conducted for the project using activated carbon pretreated with 6000 ppm Cu.

FUTURE WORK

With Task 1 essentially complete except for ongoing library search activities, Task 2 is expected to be completed next; however, due to the lack of adsorption in the current experiments, Task 2 may take longer than anticipated but should be completed by the next reporting cycle with the effect of pH and temperature being examined in detail. Other parameters will also be examined to see if their effects on the process are also critical such that a factorial design experiments will be conducted to model and optimize the process using StatEase software. This will then allow Task 3 to commence along with Task 6. Task 3 may be completed by the next reporting cycle; however, Task 6 will not. Task 3 involves maximizing gold adsorption and therefore will likely follow StatEase testing as well. Task 6 will commence next summer with Dr. Greg Hope at Griffith University in Australia by the graduate student via a subcontract. Arrangements for his visit are being made at this time. Tasks 4 and 5 will commence then as well but will not be examined in detail until the student returns from the trip.

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PUBLICATIONS/PRESENTATIONS

Not applicable at this time.

Appendix 19: Thiosulfate As A Replacement For Cyanide In The Presence Of Activators (NV003)

TECHNICAL PROGRESS REPORT

Contract Title and Number
Establishment of the Center for Advanced Separation Technologies (DE-FC26-02NT41607)

Period of Performance
Starting Date: 6/1/05
Ending Date: 10/31/2007

Sub-Recipient Project Title:
Thiosulfate As A Replacement For Cyanide In The Presence of Activators

Report Information:
Type: Semi-Annual
Number: 2
Period: 4/1/06 to 9/30/06
Date: 8/24/06
Code: NV003-R02

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ABSTRACT

Cupric ion concentration is the most important factor in this gold leaching system. Concentrations of ammonia and thiosulfate are also important, since ammonia controls the concentration of free cupric ion in solution, and thiosulfate controls the rate of reaction. Kinetic parameters for cupric ion reduction were established. An electrochemical cell has been constructed for measuring thiosulfate concentration in the presence of cupric ion.

INTRODUCTION

Background

Since its commercial implementation in 1889, cyanide has been used almost exclusively in the extraction of precious metals from ores. There are a number of reasons for this. Cyanide is very effective as a lixiviant for precious metals, and its cost is not excessive. As is well known, however, this reagent is extremely toxic, and considerable care must be exercised to prevent injury to personnel and damage to the environment during and after processing.

Another drawback to cyanide is the fact that many other toxic metals in the ores including mercury, arsenic, selenium and antimony, are also dissolved with the gold. These dissolved

secondary metals not only interfere with the extraction of gold but also pose an additional burden on the treatment of the liquid streams after extraction. Further, refractory carbonaceous ores 'rob' the pregnant leaching solution of gold values when cyanide is used as lixiviant.

For these reasons, considerable effort has been directed to developing other effective lixiviants to obviate the use of cyanide in precious metals processing. Alternative noncyanide lixiviants have been examined previously. These include: ammonia, thiourea, thiosulfate, iodine, polysulfides and malonitriles. Ammonia requires high temperature (Han and Meng 1992). The drawbacks of using thiourea as lixiviant include high reagent consumption, the formation of passive surface coatings and low leaching efficiencies. Schulze (1984, 1986) has studied SO_2/redox couple control, while Little (1987) has studied ferric sulfate and lignin sulfonate additions to counter these drawbacks. Iodide is both expensive and corrosive. Malononitriles are expensive and generate free cyanide ions (Scheiner and Lindstrom 1972).

Jiang et al. (1992) and Wan et al. (1994) reported the enhancement in leaching of gold in the presence of cupric tetrammine in ammoniacal thiosulfate solutions. In general, researchers have found that ammonium thiosulfate is a good lixiviant for gold dissolution. The problem of using this reagent, however, is the instability of thiosulfate in solution and excessive reagent loss during processing. Oxidative conditions are essential for the dissolution of gold, and under these conditions, thiosulfate is oxidized to tetrathionate. Therefore, the development of reaction conditions is needed which can increase oxidation of gold while keeping thiolsulfate losses minimal.

Objective and Approach

The objective of this work is to improve and optimize thiosulfate leaching of gold so that a new viable technology can be used to replace cyanide leaching in precious metals extraction. To realize this objective, the following studies will be made:

- A study and development of chemical conditions under which the degradation of thiosulfate is minimized.
- A study and development of chemical conditions under which the oxidation kinetics of gold dissolution are increased.
- Use of developed process to leach oxide and low-grade carbonaceous gold ores.

PROJECT TASKS

Gold Leaching/Chemical Conditions

The effect of ammonium hydroxide and thiosulfate concentrations with constant copper concentration on gold leaching was investigated. As shown in Figure 1, at lower concentration of NH_4OH (0.1M), gold dissolution rate decreases with increase of $(NH_4)_2S_2O_3$ addition. However, at a higher concentration of NH_4OH (0.5M), gold dissolution increases with thiosulfate concentration (Figure 1). These results can probably be explained on the basis that greater

complexation of Cu^{2+} to $Cu(NH_3)_4^{2+}$ will occur with the higher $NH_4(OH)$ concentration which would result in greater gold dissolution and lesser oxidation of thiosulfate by cupric ion.

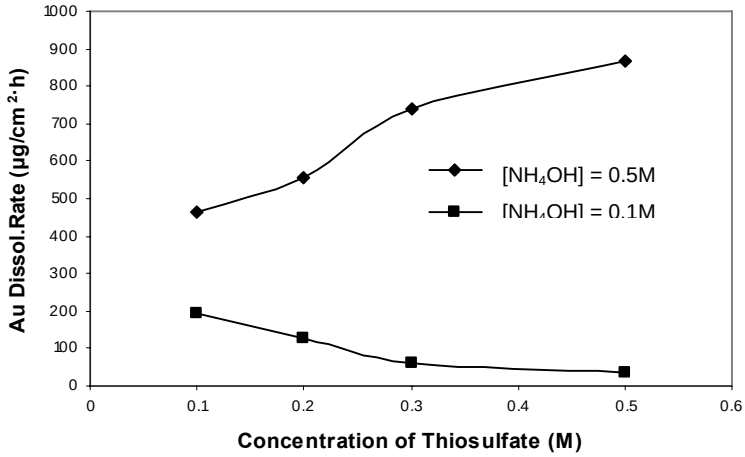

Figure 1. The interaction of ammonium hydroxide and thiosulfate. Conditions: Cu^{2+}, 0.008 M; T=22°C; leaching time, 2.0 hr.

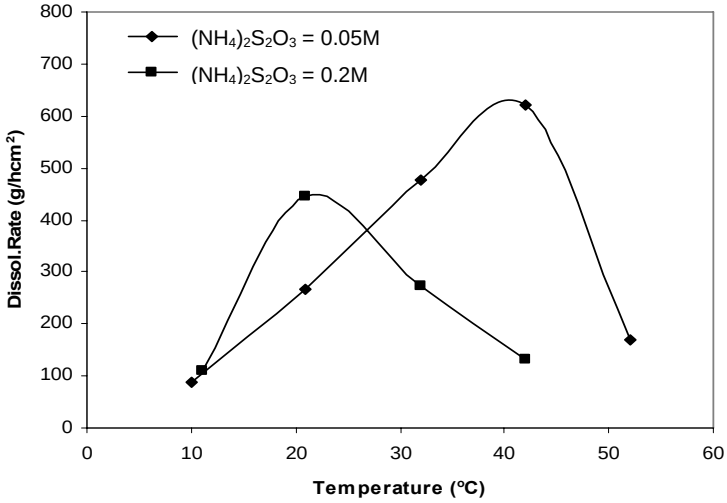

Figure 2. Effect of temperature and thiosulfate concentration on gold leaching. Conditions: Cu^{2+}, 0.008 M; NH_4OH, 0.2 M; T=22°C; leaching time, 2.0 hr.

The effect of temperature was also studied. Optimum temperature for leaching is shown to vary with the ratio of ammonium hydroxide and thiosulfate. See Figure 2. These data are explained on the basis of the kinetics of formation of cuprous thiosulfate and oxidation of thiosulfate to tetrathionate.

The reduction of Cu^{2+} and the decomposition of $S_2O_3^{2-}$ have been presented (Zhang and Dreisinger, 2002; Aylmore and, 2001). In the NH_3- $S_2O_3^{2-}$-Cu^{2+} system,

$$2Cu(NH_3)_4^{2+} + 8S_2O_3^{2-} \leftrightarrows 2Cu(S_2O_3)_3^{5-} + S_4O_6^{2-} + 8NH_3 \quad (1)$$

The general form of the rate equation is:

$$-d[Cu(NH_3)_4^{2+}]/dt = k[Cu(NH_3)_4^{2+}]^a[S_2O_3^{2-}]^b \quad (2)$$

where k is the rate constant of reaction.

Because of the concentration of thiosulfate >> [Cu^{2+}], the thiosulfate concentration may be regarded as constant. Then,

$$-d[Cu(NH_3)_4^{2+}]/dt = k_1[Cu(NH_3)_4^{2+}]^a \quad (3)$$

where

$$k_1 = k[S_2O_3^{2-}]^b \quad (4)$$

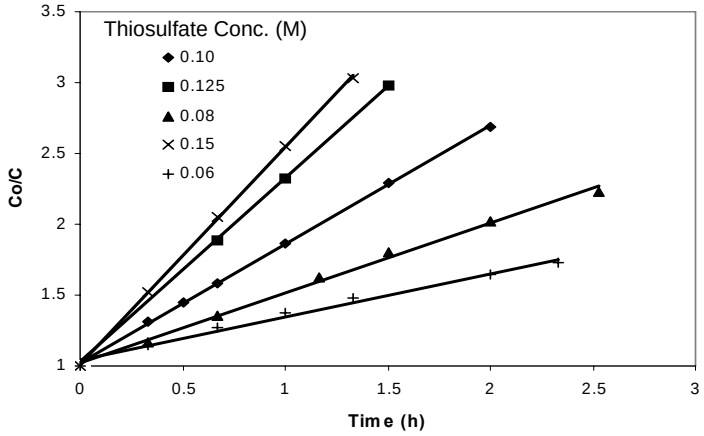

Figure 3. Cu^{2+} concentration as a function of time. Conditions: [NH_4OH], 0.5 M; [$(NH_4)_2S_2O_3$], 0.06-0.125 M; T=22^oC; leaching time, 2.0 hr. Co=0.008 M (initial concentration of cupric ion).

Figure 3 shows that the cupric concentration decreases more rapidly when the concentration of thiosulfate increases. All of the Co/C-time relationships are linear, which is indicative of second order reaction. Thus, equation (3) becomes:

$$-d[Cu(NH_3)_4^{2+}]/dt = k_1[Cu(NH_3)_4^{2+}]^2 \quad (5)$$

The apparent rate constant, k_1, can be determined from the slope of the line at a specific thiosulfate concentration in Figure 3. From these values the rate constant for the reaction and the order of reaction can be determined (Equation 4). The rate constant is 49.2, and the order of reaction for $S_2O_3^{2-}$ is 1.90.

Then,

$$-d[Cu(NH_3)_4^{2+}]/dt = 49.2\ [Cu(NH_3)_4^{2+}]^2[S_2O_3^{2-}]^{1.9}\ \text{L mol}^{-1}\ \text{h}^{-1} \quad (6)$$

Thiosulfate Analysis

Analysis of thiosulfate concentration is problematic when the solution also contains copper ion. Measuring the concentration electrochemically obviates this problem, and an electrochemical cell was constructed and tested. Reproducibility of measurements is good. Thiosulfate decomposition experiments were conducted in the NH_4OH (0.5 M) - $(NH_4)_2S_2O_3$ (0.1 M) - Cu^{2+} (0.008 M) system. Thiosulfate concentration is relatively stable under these conditions which is consistent with the assumptions used in Equation 3.

SUMMARY

These studies have shown that cupric ion concentration is the most important factor in this system. Concentrations of ammonia and thiosulfate are also important, since ammonia controls the concentration of free cupric ion in solution, and thiosulfate controls the rate of reaction.

Kinetic parameters of cupric ion reduction were established. Results show that the reduction rate increases when thiosulfate concentration increases and temperature is elevated. Experiments also show that higher concentrations of thiosulfate are necessary for gold leaching at room temperature than at higher temperature.

An electrochemical cell has been constructed for measuring thiosulfate concentration in the presence of cupric ion.

FUTURE WORK

Future work will concentrate on optimizing concentrations of cupric ions, ammonium thiosulfate, and ammonia for gold leaching. The effect of additives will also be investigated.

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R

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Appendix 20: Phytomining for Nickel and Silver Nanoparticles (WV016)

TECHNICAL PROGRESS REPORT

Contract Title and Number:	Period of Performance:
Crosscutting Technology Development at the Center for Advanced Separation Technologies (DE-FC26-02NT41607)	Starting Date: 6/1/2005 Ending Date: 10/31/2007

Sub-Recipient Project Title:	Report Information:
Phytomining for Nickel and Silver Nanoparticles	Type: Semi-Annual Number: 2 Period: 4/1/06-9/30/06
Principal Investigators:	Date: 8/31/06
Ray Y. K. Yang, Eung Ha Cho	Code: WV016-R02
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Ray Y. K. Yang Chemical Engineering Department West Virginia University Morgantown WV 26506-6102	Phone: (304) 293 2111x2419 Fax: E-Mail: ryang@mail.wvu.edu
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No subcontracts issued	Phone: Fax: E-Mail:

ABSTRACT

Silver nanoparticles were produced from the leave extracts of three cultivars of geranium. The bio-formation process was found to be rapid, achieving high concentrations of silver nanoparticles in about 15 to 24 hours. Light was required for the bio-reactions involved, while exposure to oxygen appeared to have no significant effect. The nanoparticles produced were found to remain stable for several months. The intra-cellular contents of silver in stevia cells cultivated in suspension cultures and in the sprouts of mung bean and alfalfa are noticeably enhanced, overall, as the silver concentrations in contact with the plant cells or the sprouts increase, confirming the extraction and transportation of silver ions into the cells of the plants tested. In addition, the contents of silver in cells cultivated in suspension cultures are, in general, higher compared to that in sprouts.

INTRODUCTION

Background

Phytomining is the production of a metal by growing high-biomass plants that hyper-accumulate high concentrations of a target metal. A conventional phytomining operation would consist of planting a hyperaccumlator crop over a low-grade ore body or mineralized

soil, followed by harvesting and incineration of the biomass to ash to produce “bio-ore”. In this project, we have expanded conventional phytomining to include other forms of plants, notably sprouts and plant cells.

There are over 300 species of known natural nickel hyperaccumulator, with *Alyssum murale* and *Alyssum corsicum* being considered as the two top performers. From these two species, two cultivars, *Alyssum murale Waldst & Kit* and *Alyssum corsicum Duby*, were developed by Inco and collaborators [1]; their bio-ores were found to contain up to 30 % nickel by dry matter, as compared to the nickel ores, which usually contain only 2-5% nickel. Since revegetation of mined area has to be done anyway, it is believed that in the near future phytomining for nickel will become competitive to open pit mining and deep mining [1].

Leaf extract of geranium (*Pelargonium graveolens*) treated with silver nitrate solution were used recently for rapid biosynthesis of stable silver nanoparticles [2]. The nanoparticles were found to be predominantly spherical ranging from 16 to 40 nm with average size of approximately 27 nm. It was speculated that proteins and/or terpenoids in the geranium leaves caused the biosynthesis of silver nanoparticles as well as their stabilization.

Gardea-Torresdey and co-workers [3, 4] were the first to use X-ray absorption spectroscopy (XAS) and transmission electron microscopy (TEM) to show the existence of gold and silver nanoparticles in live alfalfa sprouts grown on agar-agar treated, respectively, with potassium tetrachloroaurate and silver nitrate. They found that the nanoparticles produced by the bean sprouts are in random shapes, but may be made more uniform by changing the acidity of the solid growing medium. However, to the best of our knowledge, no scanning probe microscopy studies of surface characteristics of silver nanoparticles formed in bean sprouts have so far been reported in the literature, nor are the existences of silver nanoparticles in plant cells grown in suspension cultures.

Objective

The objective of this project is to show the existence of nickel and silver nanoparticles in a few carefully selected species of plants in various forms including their ashes, and to study the sizes, shapes, surface characteristics, and other pertinent features of the nickel and silver nanoparticles formed therein.

PROJECT TASKS

Task 1 − Investigation of silver nanoparticles by geranium

A series of exploratory experiments were conducted with the ruptured leaves of three cultivars of scented geranium, “Rober’s Lemon Rose” (RR), “Rose”(R), and “Lady Plymouth” (LP), to investigate the factors affecting extra-cellular formation of silver nanoparticles in the broth of geranium leaves. Our major finding during this period is that light is the dominating factor in the rapid bio-formation of silver nanoparticles, while exposure to oxygen appears to have no significant or obvious effect. The nanoparticle forming reaction is rapid, as indicated by the fast increase in the intensity of the color of the broth with time soon after the addition of dilute silver nitrate solution. Exposing to light, the

reaction appears to be completed in about 15 to 24 hours. However, in darkness, no sign of reaction taking place can be detected until the mixture is exposed to light. The final color of the mixture indicates extremely high concentration of silver nanoparticles.

Shown in Figure 1.1 are the colors of the final mixtures with 20 time dilution so the color differences between species, if any, may be detected. The three long vials shown in the picture on the left are the same vials shown in the photo on the right. In the latter, bottles having much larger diameters than the vials and containing exactly the same mixtures as in the corresponding vials are added to show the slight variations in colors due to different lengths of light paths.

Figure 1.1 Colors of aqueous solution of silver nanoparticles produced from three cultivars of geranium: "Rober's Rose" (RR), "Rose"(R), and "Lady Plymouth" (LP)

All the colors above are yellowish-brown, considered as the typical color of predominantly spherical silver nanoparticles in water [2]. Spectrophtometer measurements of the samples of 20X diluted final mixtures show that the silver surface plasmon resonance bands occur at approximately 421, 410, and 413 nm, respectively, for R, RR, and LP. These values are quite close to the value of 440 nm reported in the literature for an unknown cultivar of geranium [2]. No observable changes in the colors of the samples of the 20X diluted final mixtures were detected even after several months of storage exposing to light, indicating that the silver nanoparticles produced are very stable. As clearly indicated in the photo above on the left, the differences in color among the three cultivars studied in this task are not significant.

Task 2 – Investigation of silver nanoparticles in bean sprouts

During this project period, both mung bean (*Vigna radiate*) and alfalfa (*Medicago sativa*) were grown in both type-A and type-S sprouters containing silver nitrate to study intra-cellular formation of silver nanoparticles in these two types of sprouts. In the S-sprouter both mung bean and alfalfa are grown in the same container side by side and only the roots of the sprouts are in contact with the sprouter solution. On the other hand, the A-sprouter periodically sprinkles all parts of the sprouts with sprouter solution. Shown in Figures 2.1 and 2.2 below are the silver contents (in mg silver per gram of dry biomass) of sprouts germinated and grown in four different concentrations (10, 20, and 40 ppm of silver, with zero as control) of sprouter solution for seven days in both types of sprouter.

Figure 2.1 Dependence of silver concentrations in mung bean and alfalfa sprouts on silver concentrations in sprouter solutions for type A sprouter

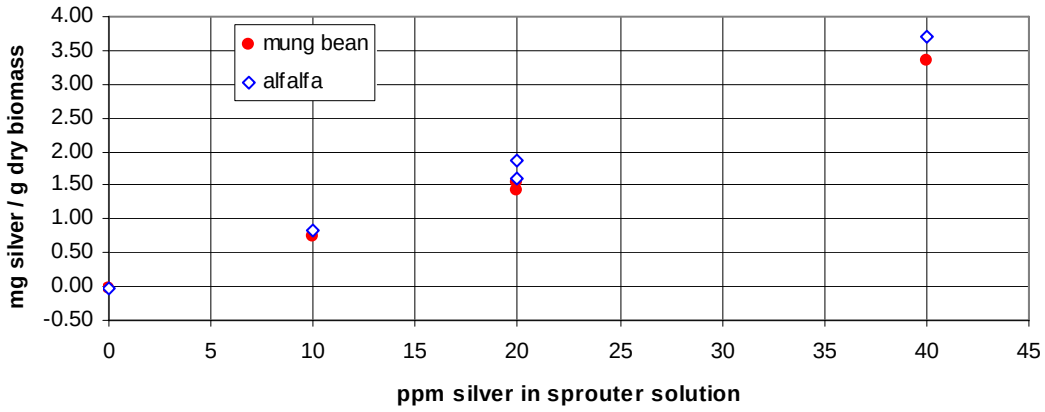
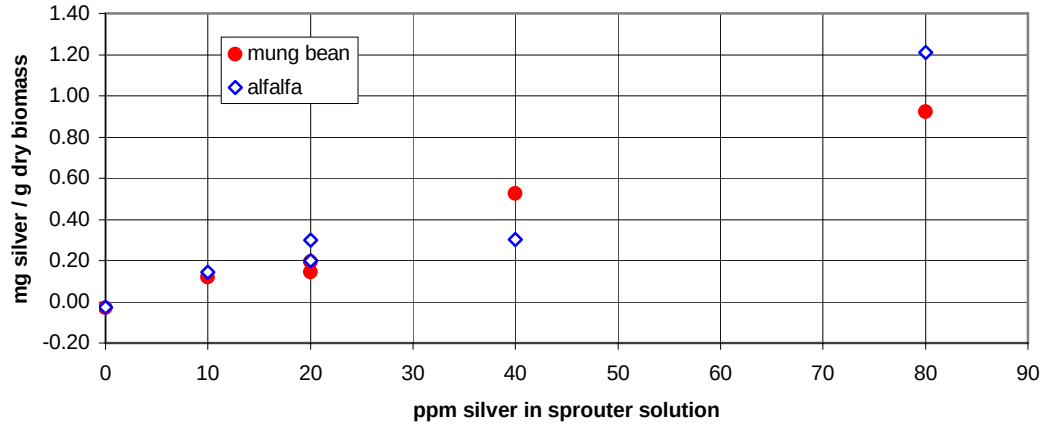


Figure 2.2 Dependence of silver concentrations in mung bean and alfalfa sprouts on silver concentrations in sprouter solutions for type S sprouter



The data collected so far clearly indicate that intra-cellular contents of silver increase with increasing concentrations of silver in the sprouter solution for both species of sprout and for both types of sprouter. The higher silver content in A-sprouter may be as a result of the exposure of all parts of sprouts to the silver-containing sprouter solution.

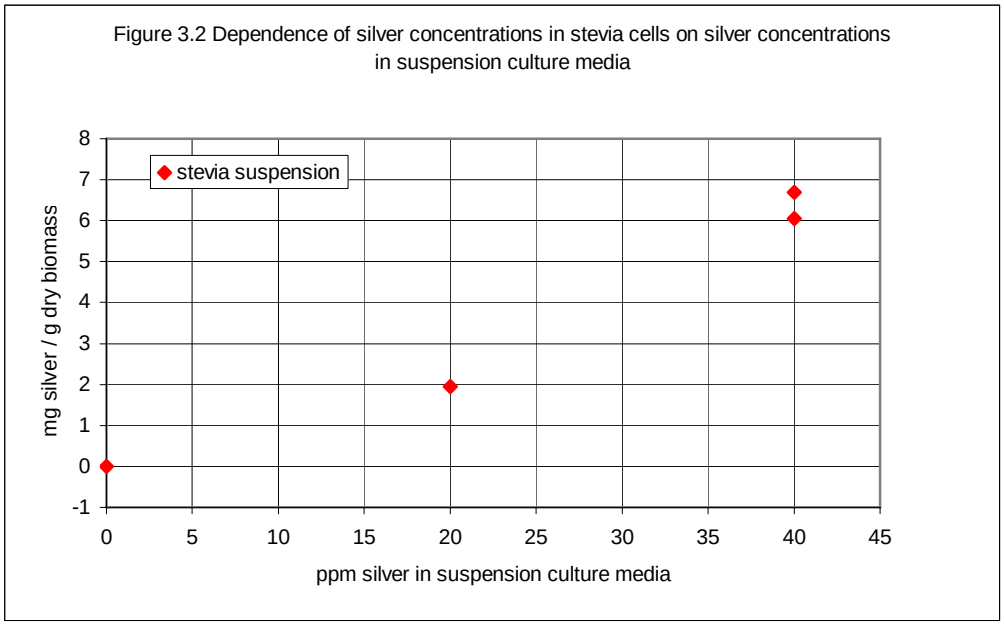
Task 3 – Investigation of silver nanoparticles in plant cells

Subculturing of callus cultures of periwinkle (*Catharanthus roseus*), red beet (*Beta vulgaris*), and stevia (*stevia rebaudiana*), which were established in previous project period, was continued during this project period. In addition, using agrobacterium, *A. rhizogenes*, we have developed hairy root culture of stevia starting from seeds. It has so far been sub-

cultured several times. Shown in Figure 3.1 below are the hairy root cultures of stevia five weeks after its first subculture; shown on the left was grown in darkness, while the one on the right in 12/12 light/dark cycle. Culture grown in the dark appears to grow at a faster rate. The hairy root cultures of stevia (one in dark and one in light) developed will be used in suspension culture to study intracellular formation of silver nanoparticles. It is well known that hairy root cultures are genetically much more stable than callus cultures.

Figure 3.1 Hairy root cultures of stevia five weeks after first subculture

The three callus cultures and the one hairy root culture, currently maintained in solid media, are the source of suspension cultures (in liquid media) for studying intra-cellular formation of silver nanoparticles in the three species of plant cells mentioned above. Shown in Figure 3.2 below is a plot of concentrations of silver (in mg silver per gram of dry cell mass) in stevia versus ppm of silver in liquid suspension culture medium.



The limited data collected so far clearly indicate that intra-cellular content of silver increases with increasing concentration of silver in the medium. Although plant species are different, silver contents in plant cells grown in suspension culture are again higher than that in the sprouts shown in Figures 2.1 and 2.2. We reported similar observation in the case of gold nanoparticles.

SUMMARY

Silver nanoparticles were produced from the leave extracts of three cultivars of geranium. The bio-formation process was found to be rapid, achieving high concentrations of silver nanoparticles in about 15 to 24 hours. Light was required for the bio-reactions involved, while exposure to oxygen appeared to have no significant effect. The nanoparticles produced were found to remain stable for several months. The intra-cellular contents of silver in stevia cells cultivated in suspension cultures and in the sprouts of mung bean and alfalfa are noticeably enhanced, overall, as the silver concentrations in contact with the plant cells or the sprouts increase, confirming the extraction and transportation of silver ions into the cells of the plants tested. In addition, the contents of silver in cells cultivated in suspension cultures are, in general, higher compared to that in sprouts.

FUTURE WORK

Future experimental work to be conducted include: (1) To continue our investigation on the extra-cellular formation of silver nanoparticles by geranium; (2) To grow nickel-hyperaccumulator plants, *Alyssum murale Waldst & Kit* (or *Alyssum murale*), *Alyssum corsicum Duby* (or *Alyssum corsicum*), and *Alyssum bertolonii*, and study the nickel nanoparticles formed in those plants; (3) To initiate and develop callus cultures of geranium and *Alyssum spp.*; the former has just been started; (4) To continue and expand our investigation on intracellular formation of silver nanoparticles in suspension cultures of geranium, *Alyssum spp.,* stevia (both hairy root and cell), beet, and periwinkle; and (5) To continue our investigation on silver nanoparticles formed in the sprouts of mung bean and alfalfa.

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Appendix 21: Online Monitoring and Diagnosing of Coal Fines During Separation Process (WV008)

TECHNICAL PROGRESS REPORT

Contract Title/Number:	Period of Performance:
Crosscutting Technology Development at the Center for Advanced Separation Technologies (DE-FC26-02NT41607)	Starting Date: 5/15/03 Ending Date: 10/31/06

Sub-Recipient Project Title:	Report Information:
On Line monitoring and diagnosing of coal fines during separation process using LIBS. Principal Investigators: Dr. Bruce Kang, WVU Dr. Eric Johnson, WVU Contact Address: Dr. Bruce Kang 353 Engineering Science Building Evansdale Campus, WVU Morgantown, WV 26506 Subcontractor Address: No subcontracts issued	Type: Semi-Annual Number: 7 Report Period: 4/1/06-9/30/06 Date: 9/26/06 Code: WV008-R07 Contact Phone/e-mail: Phone: (304)-293-3111 x2316 Fax: Email: Bruce.Kang@mail.wvu.edu Subcontractor Information: Phone: Fax: E-Mail:

ABSTRACT

This research project investigates a fundamental study of applying Laser Induced Breakdown Spectroscopy (LIBS) to coal samples and coal fines. Apparatus and methodology were developed to quantify the content of carbon, sulfur, iron and mercury in coal. A list of the most sensitive emission lines for the elements of carbon, iron, mercury and sulfur were composed. The spectrograph was tuned and LIBS tests were done on each respective element. It was observed carbon and mercury could be quantified using LIBS. A scanning mirror was added to the LIBS apparatus to observe dynamic lifetimes of emission lines. The data showed that each emission line showed different lifetimes within the laser spark.

INTRODUCTION

Laser Induced Breakdown Spectroscopy (LIBS) is a technique that uses a powerful laser to ablate a sample of a desired material. This ablation causes a plasma formation in which the material is broken down into excited ionic and atomic states. The atoms then emit characteristic optical radiation known as an emission spectrum. Collection of the emitted light can be used to provide information on the elemental composition of the material.

Of particular interest of this research is the detection and quantitative measurement of the amount of carbon, sulfur, mercury, and other trace elements in the separated coal fines. In the previous progress report, we have provided test results of static and dynamic LIBS data of coal samples. In this report, we'll show some more details of the LIBS test apparatus

development for dynamic LIBS using a scanning mirror to observe dynamic lifetimes of emission lines.

PROJECT TASKS

1. Experimental Apparatus

The experimental LIBS apparatus was designed and built to allow optimum signal collection as well as temporal characteristics of the LIBS spark of coal. A two channel pulse generator (BNC 555) was used to control the synchronization of the experiment. When the pulse generator was activated, channel A sent a signal to the flash lamp of the laser (Quanta Ray DCR 11 Q-switched Nd: YAG). Approximately 250 microseconds after the signal was sent to the flash lamp, the laser fired. The laser beam was focused through a focusing lens (CVI Laser, focal length = 100mm, diameter = 25.4mm) onto a pellet, creating a plasma spark. The CCD controller was connected to output channel B of the pulse generator.

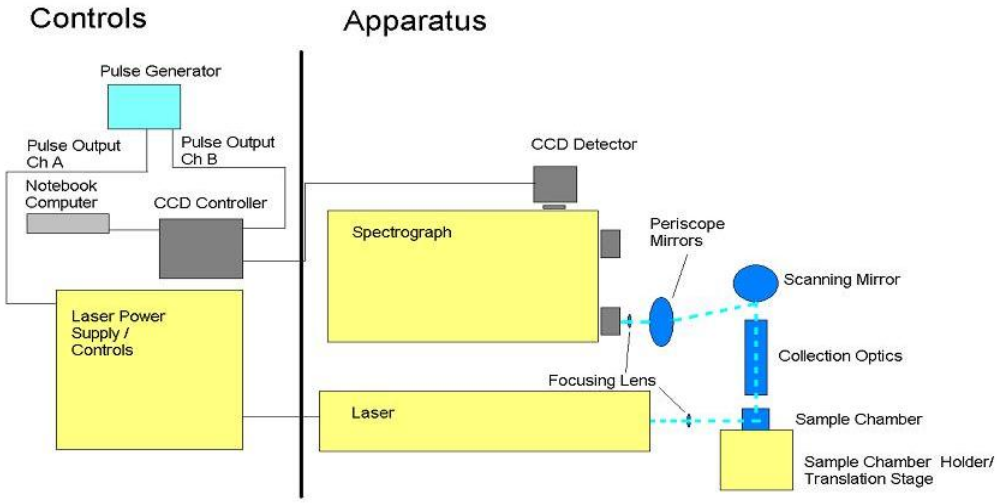

Figure 1- LIBS Testing Schematic

Comment [NETL1]: When this is printed in B/W, it doesn't come up as well as in color. Suggestion: since the Pulse generator, CCD controller, and laser power supply are all electronic devices, why not make them all dark gray? Also, the use of blue on blue for the optical path could be improved. Experiment a little with it.

Once the laser spark occurred, the light was collected and collimated by a modular collimator system (designed and constructed in-house with components purchased from Thor Labs). The modular collimator consists of a collection lens (focal length = 100mm, lens diameter = 25.4mm), a focusing lens (focal length = 100mm, lens diameter = 25.4mm), a pinhole (diameter = 400 μm), and a collimation lens (focal length = 35mm, lens diameter = 25.4 mm). The collimated light traveled to the polygonal scanning mirror (Lincoln Laser Company), where it was reflected off one of the scanning mirror facets. The light then traversed through a set of periscope mirrors, and was reflected onto a focusing lens (focal length = 50mm, diameter = 25.4mm). The lens focused the collimated light down onto the entrance slit to the

spectrograph (Horiba Jobin-Yvon HR640). Depending on whether the scanning mirror was enabled (moving) or disabled (stationary) there was either a line or a focused spot on the entrance slit of the spectrograph.

Comment [NETL2]: This is a transition sentence into the next paragraph. It needs some wordsmithing to clean it up.

2. Static and Dynamic LIBS

When the scanning mirror was turned off, data from the LIBS spark was taken with no internal gating. Also, because of a lack of a shutter on the CCD camera, the CCD camera was fully exposed until the data was completely read out, which was approximately 2.6 seconds. The image formed by the spark created a spot on the entrance slit. This spot encompassed the entire lifetime of the laser-induced plasma, from the black body radiation observed in initial plasma formation to the emission lines resulting from the recombination of atoms and molecules. This process was deemed "static LIBS".

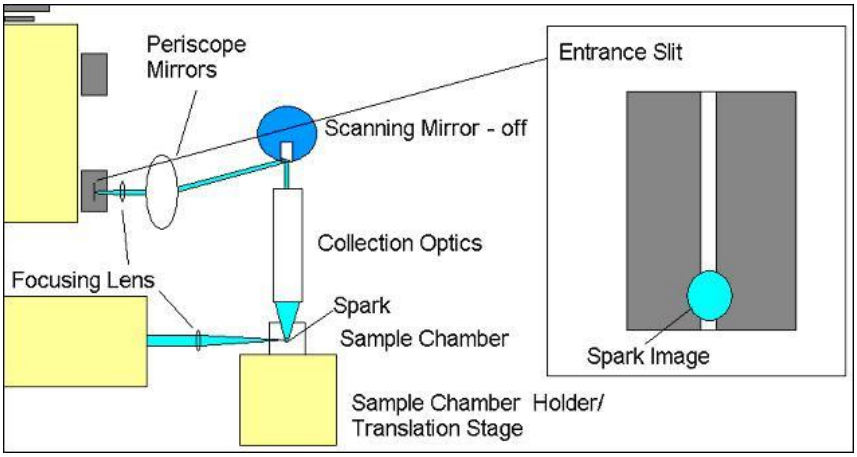

Figure 3 – "Static" LIBS

When the scanning mirror was enabled, the image of the spark was spread out across the entrance slit because of the mirror's motion. This created a line on a portion of the entrance slit. Each point in the line represented a different time within the lifetime of the spark. This information provides us with an approximate time frame to observe the temporal behavior of each emission line. This process was named "dynamic LIBS".

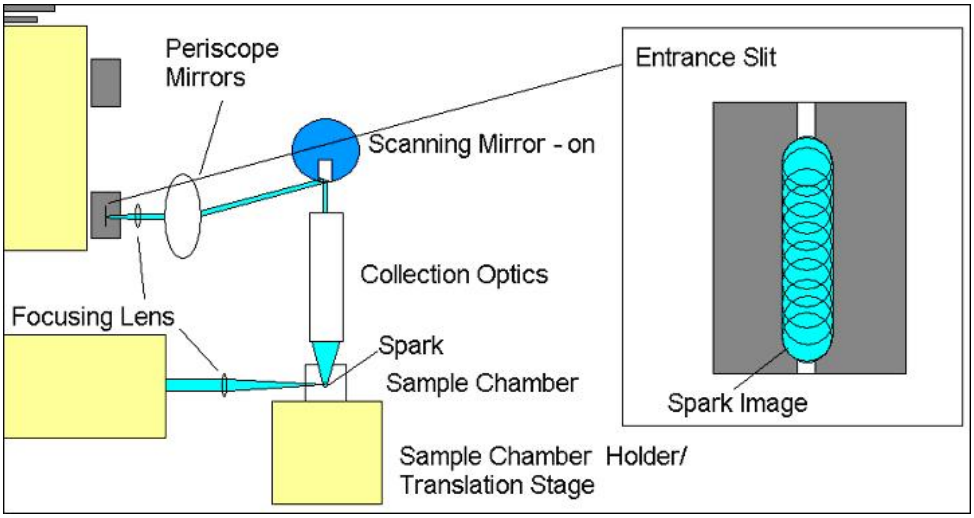

Figure 1 – "Dynamic" LIBS

3. LIBS Testing Procedure

During startup, the laser, computer, detector controller and pulse generator were turned on, the overhead ceiling light (which contained mercury) wsa turned off, and the software (Winspec32) was opened. Channel B on the pulse generator was delayed by 250 microseconds compensate for the delay time between the pulse to the flash lamp from channel A and the actual laser firing.

The specimen holder with a mercury lamp was aligned to the optics via a translation stage. The mercury lamp emitted light through a pinhole (diameter = 250 μm) at the approximate spark location. The mercury lamp, because of its intensity, made an excellent alignment tool.

During spectrograph calibration, which followed alignment, the pinhole was removed and replaced with a sample chamber, which was a 2"x2"x2" cube constructed in-house using components from Edmund Optics and Mountaineer Glass & Mirror Company. The sample holder contained iron powder for calibration of the spectrograph.

To perform spectrograph calibration, a LIBS spectra of iron powder with the ceiling lights on was obtained to observe iron and mercury emission lines. The spectrograph was then tuned to a selected wavelength range, and calibrated using a linear relationship between known emission lines of iron and mercury. This step was only necessary when selecting the desired wavelength range to be observed.

Once the calibration specimen was removed, the pinhole was placed over the lamp source and the alignment was repeated. After re-alignment, the pinhole was removed and a sample chamber with a test specimen was placed in the sample holder.

Comment [NETL3]: Look at how this makes the sentence more efficient.

The spinning mirror was either turned on or left off, depending of the desired test. The mirror was left off for static LIBS testing, and turned on for dynamic LIBS testing. Pulse generator triggered the flash lamp to the laser (channel A) as well as the CCD controller (channel B). The collected light traversed through the pinhole into the modular collimated system. If the light from the spark did not go through the pinhole, then the sample holder was appropriately translated until the light collected from plasma emission was focused through the pinhole. For dynamic LIBS testing, the spinning mirror functioned independently from the pulse generator and was not synchronized to the rest of the apparatus. As a result, a "brute force" method of testing was required to acquire data in which the laser was fired repeatedly until signal was collected. The test results conducted thus far were reported in our previous progress report.

Comment [NETL4]: How did this determine anything? This is a dependent action based on your determination of what type test you want to run.

Comment [NETL5]: Off perhaps?

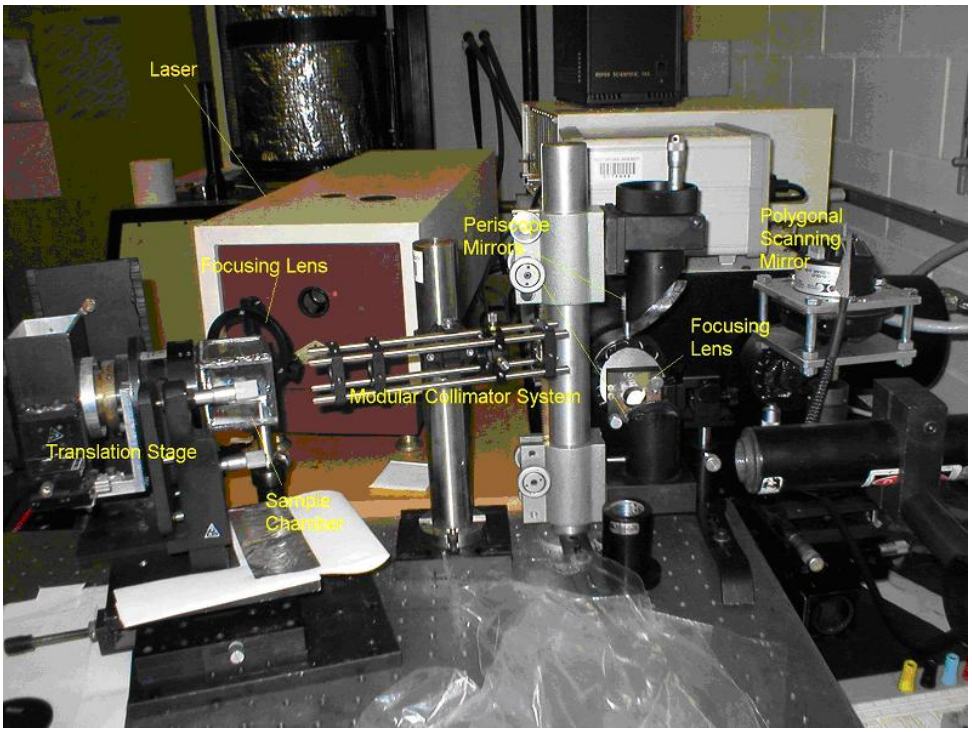

Figure 2 – LIBS Testing Apparatus

CONCLUSIONS

A dynamic LIBS system has been developed to detect C, Fe, and Hg in coal. Significant information has been obtained in analyzing the signals. Based on qualitative and semi-quantitative analysis, dynamic LIBS testing provides basic information on the lifetime and temporal characteristics for individual emission lines. Our test results (as reported earlier in the previous progress report) showed that Mercury seems to have a more sudden decay, while carbon and iron show a slight delay before actual decay occurs. The data upon observation of emission lines of one specie compared to another suggests that emission lines posses differing temporal characteristics.

FUTURE WORK

System Improvements

The sensitivity and accuracy of the LIBS method developed within the scope of this research can be improved upon. This research has shown that all of the elements of interest have the possibility of being quantitatively analyzed much faster than the traditional ASTM methods. Because of the limited detection of mercury and sulfur within the synthetic coal mixtures, future work should be focused on the development of the sensitivity limits and the synchronization of the current LIBS system.

Because of the effects of oxygen quenching mercury and sulfur emission lines, a vacuum environment or an inert gas environment could be created to enhance LIBS signals. To further enhance the signal, the CCD detector could be replaced by an Intensified CCD (ICCD) camera. An ICCD camera with time gating capabilities can be up to one thousand times more sensitive than a regular CCD camera. If the ICCD camera is used as a detector, and the samples are placed in a vacuum environment, the current LIBS apparatus could attain sensitivity in the part per billion range.

Dynamic LIBS testing gives us qualitative data of how different emission lines behave. The analysis of the dynamic LIBS signals allowed for observations of time-dependent characteristics of different emission lines. Because the system was not synchronized, a “brute force” method was relied upon to obtain usable dynamic LIBS signals. Synchronization of the spinning mirror in conjunction with the laser and the CCD camera would be necessary for commercialization of this apparatus. Anomalies in the dynamic LIBS data were observed. A further study of these anomalies will allow for a better understanding of the temporal behavior of the emission lines and the laser-induced plasma.

Appendix 22: Portable Sensor for Detecting Mercury and Other Heavy Metals Encountered In Coal Processing and Utilization (WV013)

TECHNICAL PROGRESS REPORT

Contract Title and Number:	Period of Performance:
Crosscutting Technology Development at the Center for Advanced Separation Technologies (DE-FC26-02NT41607)	Starting Date: 6/01/2004 Ending Date: 10/31/2007

Sub-Recipient Project Title:	Report Information:
Portable sensor for Detecting mercury and other Heavy Metals Encountered in Coal Processing and Utilization	Type: Semi-Annual Number: 04 Period: 04/01/06 to 09/30/06
Principal Investigator: M. S. Seehra	Date: 08/31/06 Code: WV013-R04
Contact Address:	Contact Information:
Physics Department 210 Hodges Hall West Virginia University Morgantown, WV 26506-6315	Phone: 304-293-3422 x1473 Fax: 304-293-5732 E-Mail: mseehra@wvu.edu
Subcontractor Address:	Subcontractor Information: N/A
No subcontracts issued.	Phone: Fax: E-Mail:

ABSTRACT

During this reporting period our focus remained on addressing the "reproducibility" issue of the calibration curves for mercury (Hg) detection. New BDD (boron doped diamond) electrodes were acquired and installed with assistance from Pine Instruments. Since we encountered the same "reproducibility" problem in laboratory tests with the new electrode also, the whole issue of the chemistry of "deposition" and "stripping" used in the calibration curves is being investigated. It was discovered that gold(Au) solution used for capturing Hg as an amalgam during the test contains about 10% copper(Cu) as impurity. Experiments are now underway to assure that not only Hg and Au but also Cu are stripped off after each experiment so that the electrode is "clean" for the next test. Some details of these on-going experiments and related calculations are described here along with future plans. These experiments were carried out by graduate assistant Sukanya Ranganathan under daily consultations with the PI (M.S.Seehra).

INTRODUCTION

Background

The question of accuracy and sensitivity for the detection of Hg in the ppb to ppt range using BDD electrodes was successfully addressed in our published work (Manivannan et al,2005) in that the results on Hg concentrations obtained by our technique agreed well with those obtained by CVAAS (Cold Vapor Atomic Absorption Spectroscopy). However, the problem of "reproducibility" of the calibration curves using the same BDD electrode for Hg detection for successive runs remained(Manivannan et al,2005). As shown in Fig.1, the slope of the current vs. Hg concentration for different runs is different, thus requiring a new calibration curve for each determination of Hg in an unknown sample. In practical situations, this procedure will be quite time consuming.

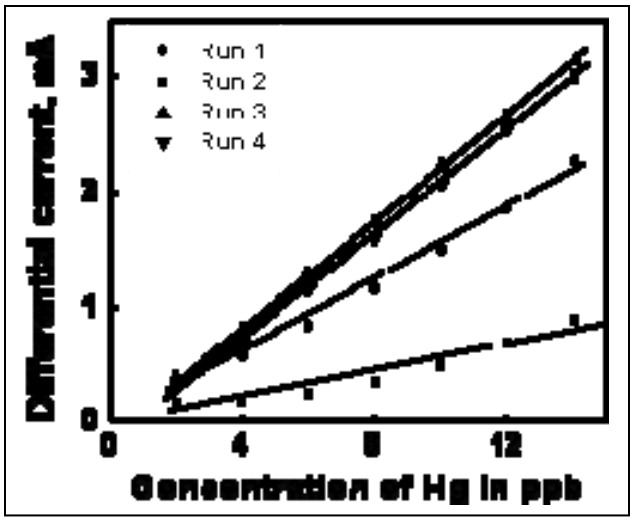

Fig.1 Four consecutive DPV calibration plots for 2-14 ppb of mercury concentrations in 1M KCl (pH 4). A 3 ppm of Gold standard solution was added; deposition time = 60s; deposition potential = -0.1 V vs. SCE; rotation speed=2000 rpm. Runs 3 & 4 were performed consecutively on the same day.

In experiments involving detection of Hg, a gold (Au) solution is added in the electrolyte (Fig.1) in order to capture Hg from the solution since Hg easily forms an amalgam with Au. We purchased a new set of BDD electrodes from Harris International Inc. and had one of them installed on our rotating disk electrode using the technical capabilities of Pine Instruments. In initial experiments with this electrode, we encountered the same "reproducibility" issue as shown in Fig.1. This led us to carefully reexamine the whole process of "deposition" and "stripping" used in developing the calibration curves (Fig.1) and used in the determination of Hg. Perhaps, the issue of "reproducibility" is really connected with the possibility that we are not able to completely strip and clean the electrode after each run, thus affecting its sensitivity in a subsequent run. As shown in the caption to Fig.1, the Hg-Au amalgam is first deposited on BDD electrode by setting the voltage at a negative value (-0.1 V) relative to where Hg is stripped off (+0.35 V) in a subsequent sweep of the voltage from -0.1 V to 0.5 V (see the data of Fig.2 acquired using the new electrode).

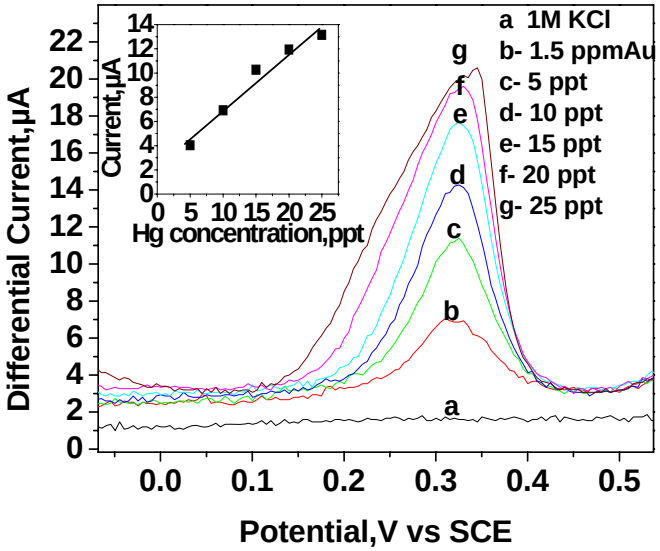

Fig2. DPV scans and calibration curves for 5ppt to 25ppt Hg^{2+} concentrations in 1M KCl (pH1). 1.5ppm gold standard solution was added; deposition time = 300sec; deposition potential = –0.1V vs.SCE;

Objectives and approach:

As a first step in this review process, we changed the deposition potential from -0.1 V to -0.2 V and then -0.4, and changed the strip scan range from -0.4 V to + 1.0 V. The purpose here was to see whether other impurities or species might be present or detected. When the deposition potential was changed to -0.4 V, followed by a stripping scan, a strong peak appeared at -0.21 V which did not change significantly as Hg concentration is changed from 100 ppt to 500 ppt (Fig.3). Surprisingly, the peak height for the -0.21 V is essentially the same without any Hg but just with 3 ppm of Au. A second peak is evident for voltages > 0.7 V. When the stripping scan range is extended to +1.2 V, the second peak becomes clearly visible centered around +0.8V (Fig.4) with peak current about ten times larger than that observed for the peak at -0.21V and the Hg peak centered around +0.35 V. So the first task was to identify these additional peaks and the develop procedures to deal with them.

PROJECT TASKS

For addressing the task of peak identification, we searched the literature for standard reduction potentials E^0 of different ions. By careful examination and calculations we arrived at the following identification using the Nernst eq.

$$E = E^0 - \frac{0.05918}{n}\log\frac{1}{M} \qquad \text{--- (1)}$$

where M is the molarity and n is the number of electrons involved in the reaction. The peak at -0.21 V is identified with the reaction

$$Cu^{2+} + 2e^- \quad \Longleftrightarrow \quad Cu(s) \quad , \quad E^0 = 0.1 \text{ V vs. SCE} \qquad \text{--- (2)}$$

To calculate E, from Fig.3 we estimate that Cu^{2+} concentration is around 200 ppt = 3.5 x 10^{-12} M and n=2 from Eq.(2). Substituting these values in Eq.(1), yields E=-0.23 V in excellent agreement with the experimental value of -0.21 V. For the reaction $Cu^{+} + e^{-} \Longleftrightarrow$ Cu(s), the calculated values of E = -0.40 V, which is about twice the experimental value.

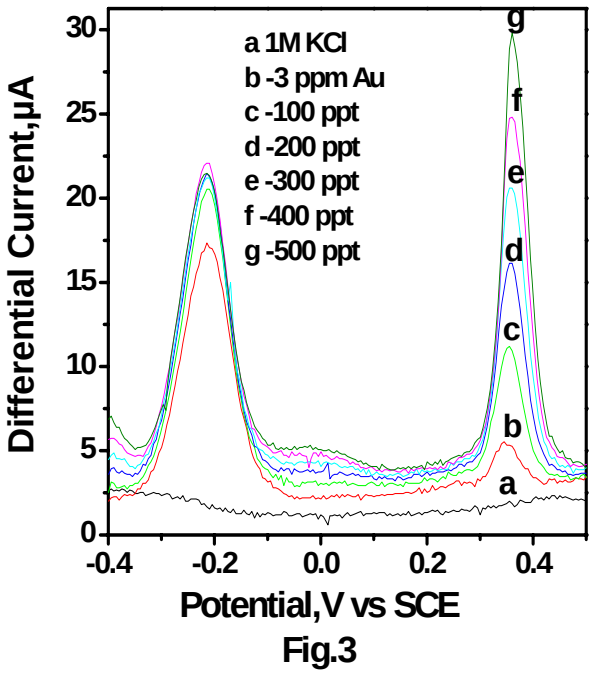

Fig.3

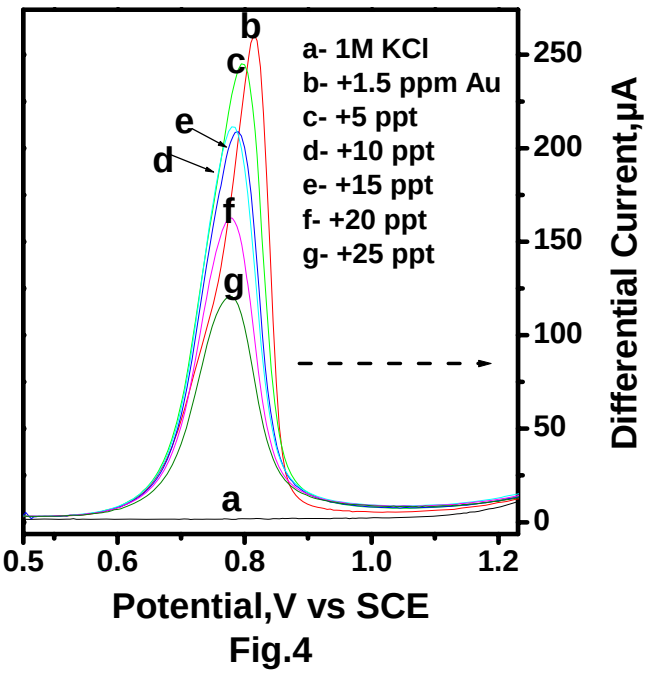

Fig.4

Fig3. DPV scans for 100ppt to 500ppt Hg^{2+} concentrations in 1M KCl (pH 1). 3 ppm gold standard solution was added; deposition time = 90 sec; deposition potential = –0.4V vs. SCE

Fig4. DPV scans for 5ppt to 25ppt Hg^{2+} concentrations in 1M KCl (pH 1). 1.5 ppm gold standard solution was added; deposition time = 300 sec; deposition potential = –0.1V vs. SCE

For Hg, 100 ppt = 4.9875×10^{-10} M. assuming the reaction to be

$$Hg^{2+} + 2e^- \Leftrightarrow Hg\ (l)\ , \qquad E^0 = 0.61 \text{ V vs. SCE} \qquad \text{--- (3)}$$

yields E = 0.35 V in excellent agreement with the experimental value of around 0.35 V in Fig.3. For Gold two relevant reactions are

$$Au^{3+} + 2e^- \Leftrightarrow Au^+\ , \qquad E^0 = 1.16 \text{ V vs. SCE} \qquad \text{--- (4)}$$

and

$$Au^+ + e^- \Leftrightarrow Au(s)\ , \qquad E^0 = 1.45 \text{ V vs. SCE} \qquad \text{--- (5)}$$

For Au, 1.5 ppm = 0.51×10^{-8} M. Substituting these values yields E^0= 0.92 V using n=2 for Eq.4 and E^0 = 0.97 V using n=1 for Eq(5). Since the final state must be Au(s), a broad peak should be centered on 0.95 V vs. SCE is predicted. In Fig.4, the peak is observed near 0.82 V slightly off the predicted value. Nevertheless, there is no doubt that this peak is due to gold since Au is added deliberately and the peak appears only after the addition of gold solution.

What is the source of copper? The concentration of Cu^{2+} is about 1/10 of Au. It is most likely that copper is due to impurity in gold solution. Since copper and silver in addition to gold, also forms amalgams with mercury(McAuliffe,1977), it follows that during the deposition process, any copper may also get deposited on the BDD electrode. Therefore, the stripping during the electrode cleaning process should be carried out in the

range of -0.4 V to 1.0 volt. Experiments are now in progress to follow this procedure to determine whether the "reproducibility" problem can be solved this way. These experiments have also raised the possibility to use copper and silver solutions instead of more expensive gold solutions. These experiments will be attempted in the near future.

SUMMARY

The problem of the "reproducibility" of the calibration curves for Hg detection using the same BDD electrode was investigated. A peak due to copper impurity from the gold solution used in the detection was discovered. It is suggested that in the electrode cleaning process, stripping in the range of -0.4 V to 1.0 V may result in a clean electrode for subsequent measurements. Copper or silver solution may also be used instead of the gold solution for capturing mercury in an amalgam. These experiments will be carried out in the near future.

FUTURE WORK

We plan to focus on the following issues in the near future using the information noted above. First, the voltage range for stripping during the electrode cleaning process will be extended to -0.4 V to +1.0 V covering the peak positions of copper, mercury and gold. This will be followed by repeating the calibration curves to determine their reproducibility. Second, we have placed orders for copper and silver solutions. Each of these will be tried replacing gold solution in the detection of mercury to determine if these offer significant advantages. Finally, results from the above experiments will be used to extend measurements to the PalmSens portable unit for realizing a portable detector. During these experiments, the issue of using standard addition method vs. internal standard method will also be looked into.

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PUBLICATIONS / PRESENTATIONS

A presentation was made by M.S.Seehra to DOE at NETL/Morgantown on July 25, 06 based on the results from phase I of this project entitled "Development of electrochemical sensor for monitoring heavy metals ions in coal processing and utilization".

Appendix 23: Development of Metallic Filters to Control Mercury from Coal Fired Power Plant Flue Gas (MT004)

TECHNICAL PROGRESS REPORT

Contract Title and Number:	Period of Performance:
Crosscutting Technology Development at the Center for Advanced Separation Technologies (DE-FC26-02NT41607)	Starting Date: 06/01/04 Ending Date: 10/31/06

Sub-Recipient Project Title:	Report Information:
"Determining the Effectiveness of Metallic Filters for Removing Mercury from Coal Fired Power Plants"	Type: Semi Annual Number: 3 Period: 04/01/06-09/30/06
Principal Investigators: Dr. Kumar Ganesan	Date: 08/31/06 Code: MT004-R03
Contact Address: Department of Environmental Engineering Montana Tech of The University of Montana 1300 West Park Street Butte, Montana 59701	Contact Information: Phone: 406-496-4239 Fax: 406-496-4650 E-Mail: kganesan@mtech.edu
Subcontractor Address: "No subcontracts issued."	Subcontractor Information: Phone: Fax: E-Mail:

DETERMINING THE EFFECTIVENESS OF METALLIC FILTERS FOR THE REMOVAL OF MERCURY FROM COAL FIRED POWER PLANTS

ABSTRACT

During this reporting period a plating technique developed in house was used to plate the filters. A new sponge filter material with much higher surface area per volume was attempted. This sponge, if it becomes successful, it will be more cost effective than the previous metallic based filters. The new filter media was coated with two different metal plating. The performance test was completed and the results indicated that the new sponge filter did not perform as well as the previously plated filters. The wire-mesh filters lasted over several days with over 90% efficiency while the sponge filters lasted less than two days with 90% efficiency.

INTRODUCTION

Two different metallic filters developed by Montana Tech showed great potential to remove mercury vapor from the coal-fired power plant flue gas. Several tests have been completed with different metallic filters. These tests were successfully performed at Montana Tech's

mercury laboratory as well as in the field. The laboratory task included testing individual filters, combining two different filters, desorbing spent filters and retesting for mercury removal efficiency.

Three different field tests were conducted in a coal fired power plant flue gas stream with new filters at different flow rates. Since the tested filters had limited surface area per unit volume, a new sponge with high surface area per volume was tried. The filters were plated using the in house plating system. The in house system was built for convenience and to optimize the thickness of the metal coating on the filters. In addition, it significantly reduced the cost plating cost. The performance tests were completed and the results indicated that the mercury removal efficiency did not last long compared to previous testing. Perhaps the new sponge is not coated with enough thickness to sustain the expected high performance. In the future coating time will be increased to enhance the thickness of the metal deposit. These filters then will be tested for their performance. This report highlights the progress made from March 2006 to September 2006.

Background

Mercury, one of the important air toxic metals is a high-priority regulatory concern because of its persistence and bioaccumulation in the environment and its neurological health impacts. The largest anthropogenic source of mercury in the United States is coal-fired power plants, which release 48 tons of mercury annually or about one-third of the total anthropogenic emissions[2]. As a result, coal-fired power plants are the focus of new EPA mercury regulations.

Currently, there is no effective control technology that will remove mercury from coal-fired power plants. The species of mercury present in the flue gas is determined by the chemical composition of the coal burned. Coal chlorine content is one of the main factors that affect the speciation of mercury upon combustion, mainly due to its ability to oxidize Hg^o to $HgCl_2$[4]. Other elements in the coal including sulfur, calcium, and iron impact the speciation of mercury, but to a lesser degree than chlorine. Eastern bituminous coals have high mercury and chlorine contents and produce a flue gas predominately composed of Hg^{2+}. On the other hand, western sub-bituminous and lignite coals have low mercury and chlorine contents and produce a flue gas with Hg^o as the dominant species. There is a great deal of research being conducted on the mechanisms of mercury-chlorine chemistry and other mercury speciation reactions that occur upon the combustion of coal at power plants[4].

Objective and Approach

The objective is to evaluate the ability of different metallic filters to remove mercury from contaminated air. Because of the high cost associated with the metallic filters we are investigating cost effective base media as filter media. The performance goal was to achieve mercury removal efficiencies above 90%. All the performance tests were evaluated based on how well this 90% efficiency goal is met. The goal for this period was (a) to use the in-house plating set up for plating filters, (b) to use a newer sponge which has higher surface area than the previous ones, and (c) to perform efficiency testing on the newly plated sponge filters.

PROJECT TASKS and EXPERIMENTAL SETUP

Experimental Procedures

Electroplating:

The filters were plated in an electroplating tank, which holds the electrolyte solution containing metal salts. The desired metal was deposited by means of an electric current on the filter surface. An electrode of the same metal to be plated is used as the anode and the filter to be plated forms the cathode of the circuit. When the anode and cathode in the electroplating cell are connected to an external supply of direct current, the metal at the anode is oxidized from the zero valence state to form cat-ions with a positive charge. These cat-ions associate with the anions in the solution. The cat-ions are reduced at the cathode to deposit in the metallic, zero valence state. Thus the current deposits metal on the cathode and the anode dissolves.

Mercury Removal Efficiency Testing:

A mercury generator was used to generate a known concentration of mercury vapor and it was passed through the filter at a flow rate of 5 L/min. The filter's inlet and outlet mercury concentrations were measured with a portable mercury analyzer, Mercury Tracker. The removal efficiency was calculated based on the inlet and outlet mercury concentrations. Once the mercury removal efficiency of the metallic filter dropped to 50%, the test was stopped and the filter went through thermal desorption.

Task 1: Developing In-house Plating Setup

A small laboratory scale plating system was put together to plate the filter with selected metals. During the last reporting period we completed initial plating of one metal on the metallic sponge. Several sponges were successfully plated individually with couple of metals. They are currently being tested for their performance in removing mercury.

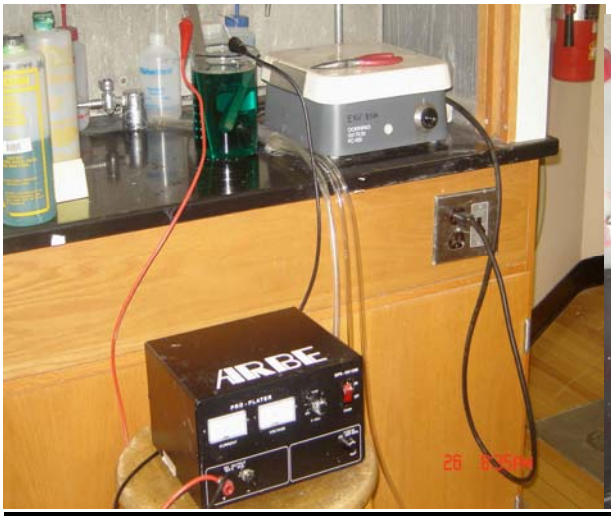

Figure 1. Plating Setup

Task 2: Substituting Higher Surface Area Filters

The second task we explored is the new sponge. The selected new sponge is light weight, and has high porosity with low pressure drop and low cost. And also this has much higher surface area per volume and therefore expected to be effective for removing mercury. This synthetic sponge is commercially available with metal coating on it. These sponges are deposited with selected metal plating.

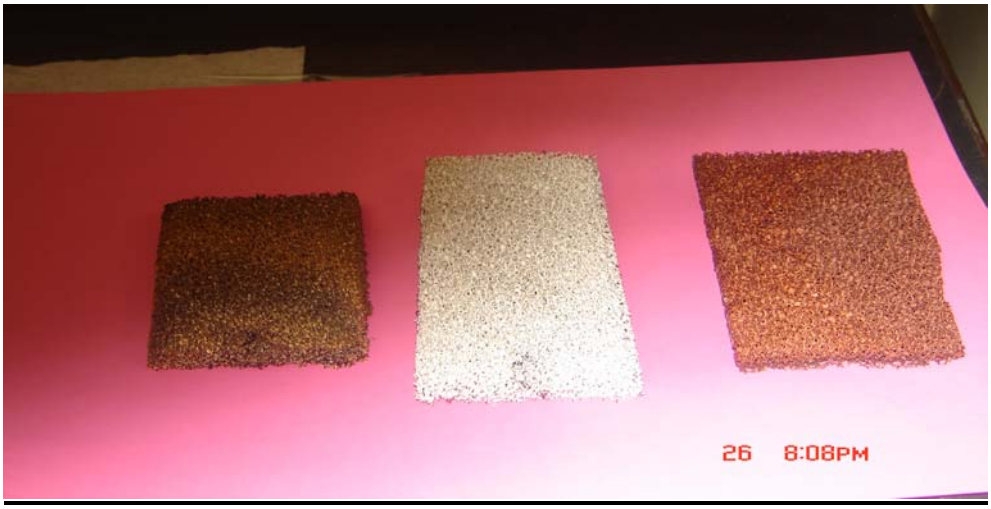

Figure 2. Newly Coated Sponges

Task 3: Filter Efficiency Testing

The newly plated sponge filters were initially tested for mercury removal efficiency as described above. The results were not successful and the removal efficiency did not last enough (less than two days compared to several days of 90% efficiency) to continue the testing. In the future in order to increase the efficiency, the coating time will be increased to enhance thickness of metal coating.

SUMMARY

In summary during this reporting period a laboratory scale in-house plating setup was established to fulfill our plating needs. A newer sponge with higher surface area was successfully plated and tested for mercury removal efficiency. The removal efficiency of the newly plated sponge was lower than expected. Perhaps the new sponge is not coated enough for high performance. Therefore to enhance the metal coating, plating time will be increased to improve the thickness of plating. This is currently being attempted.

FUTURE WORK

Future work will include continuing on optimizing the plating thickness in the sponge based filters to obtain the expected efficiency at a reasonable cost. In addition, a novel bio-nano-sponge will be made in the laboratory and plated with metals. This will be our second generation filters for mercury removal from gas streams. These bio-nano-sponges will be tested for their effectiveness with and without metallic coating. We believe that these new materials can remove mercury even without any additional metallic plating as in other filter mediums.

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PUBLICATIONS/PRESENTATIONS

The research paper was presented at the 45th 2005 PNWIS/A&WMA annual conference. Also it was submitted for the A&WMA Journal. The data was submitted and presented in an International Conference held in January 2006.

Appendix 24: Recovery of Chromium and Arsenic From Toxic Waste Stream by Reactive Polymer-Coated Absorbents (WV013)

TECHNICAL PROGRESS REPORT

Contract Title and Number:	Period of Performance:
Crosscutting Technology Development at the Center for Advanced Separation Technologies (DE-FC26-02NT41607)	Starting Date: 06/01/2004 Ending Date: 10/31/07

Sub-Recipient Project Title:
Recovery of Chromium and Arsenic from Toxic Waste Stream by Reactive Polymer-Coated Absorbents

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Department of Civil & Environmental Engineering
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Columbia, MO 65211

Report Information:
Type: Semi-Annual
Number: 4
Period: 04/01/2005 – 09/30/2006
Date: 09/30/2006
Code: WV014-R04

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ABSTRACT

Further structural characterization of iron-chitosan beads using XPS analysis was conducted and the results showed the presence of iron and arsenic in the beads when exposed to arsenic. Adsorption experiments demonstrated that iron-chitosan can be used to remove arsenic from aqueous solution. The maximum adsorption capacity increased from 1.95 mg/g to 5.97 mg/g and from 1.97 mg/g to 6.48 mg/g as the initial concentrations of arsenic increased from 0.3 mg/L to 1 mg/L for pH = 7 and pH = 8 respectively. The adsorption isotherm fitted Freundlich model well and the maximum adsorption removal efficiency was observed at pH = 9.1. Kinetic batch experiments results indicated that about 60% of the arsenic was adsorbed by the iron-chitosan within the first 30 min and pseudo-second-order model fitted the experimental data well with the reaction rate constants of 3.194×10^{-2} and 1.151×10^{-2} g mg^{-1} min^{-1} for the initial arsenic(III) concentrations of 306 and 994 µg/L, respectively.

Effect of anions on arsenic removal studies demonstrated that competition in multi-sorbate systems could significantly restrain arsenic adsorption, especially if silicate ion was present. Sulfate had only a minimal effect, while phosphate reduced adsorption considerably at pH values greater than 7 where anion adsorption sites are limited. Column studies showed that the breakthrough point was at 768 empty bed volumes (EBV) when flow rate was 25 ml/hr.

INTRODUCTION

Background

Acid mine drainage (AMD) contains high concentrations of sulfate, iron, and many other toxic elements existing in the original mineral assembly, including divalent heavy metals and oxyanions and frequently serves as a large-scale and persistent source of pollution to surface and ground waters. This study focuses on contaminants in their anionic forms (i.e., AsO_4^{3-} and CrO_4^{-}) in AMD, because these anions are highly soluble and are normally not removed by treatment processes such as lime neutralization and precipitation designed for divalent heavy metals (e.g., Cu^{2+}, Pb^{2+}, and Zn^{2+}).

Objective and Approach

Within the first three six-month reporting periods, the investigators finished Task 1, Task 2 and Task 3 on Cr(VI) removal and recovery. Task 1 and Task 2 for As removal have been initiated. In the fourth reporting period, Tasks 1, 2, and 3 for As removal were finished. The efforts included: (1) Further structural characterization of iron-chitosan beads; (2) Adsorption kinetics and isotherms; (3) Effect of anions on arsenic removal; and (4) Column study.

PROJECT TASKS

This research involves 3 tasks. Task 1 involves the development and characterization of the new adsorbents. In Task 2, the sportion under different environmental conditions will be optimized. Task 3 involves the investigation of desorption condition, recovery of Cr(VI), and regeneration and reuse of the adsorbent.

Task 1. Development of New Adsorbents for Arsenic Removal and Structural Characterization of the Absorbent.

Characterization of Iron-Chitosan Beads

Further structural characterization of iron-chitosan beads includes XPS analysis. In XPS analysis, a survey scan was used to ensure that the elemental composition at the surface is representative of the entire sample. The higher resolution utility scans also provide atomic concentration of Fe, C, N and O in the sample. Figure 1 shows the peak positions of carbon, nitrogen, oxygen, and iron obtained by the XPS for pure iron-chitosan. In Fig.1, the carbon 1s peak was observed at 283.0 eV with a FWHM (full width at maximum height) of 2.015. The N-1s peak for iron-chitosan bead was found at 398.0eV (FWHM 2.00eV), which can be attributed to the amino groups in chitosan. Table 1 shows the surface elemental concentration of C, N, O and Fe as determined from peak/area ratios, after correcting with the experimentally determined sensitive factor (±5%). The XPS analysis of iron-chitosan beads exposed to As (III) solutions show peaks of As (III), C-1s, N-1s, O-1s and Fe as shown in Fig. 2. The Binding energy and the atomic concentrations on the beads are given in Table 2.

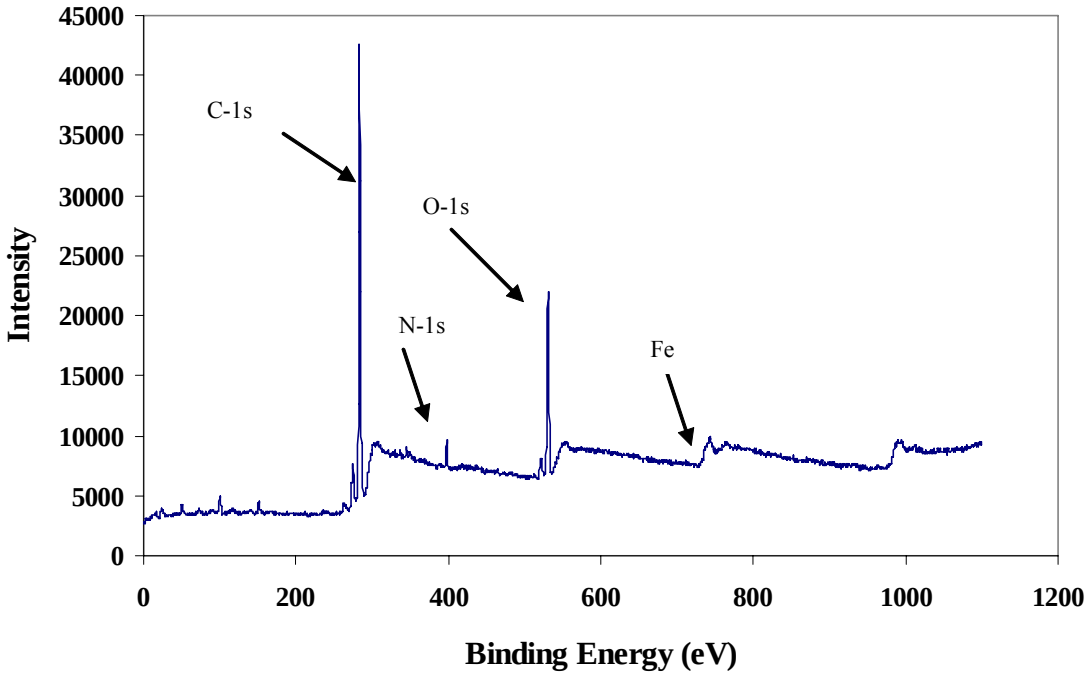

Fig. 1 XPS spectrum of pure iron-chitosan bead

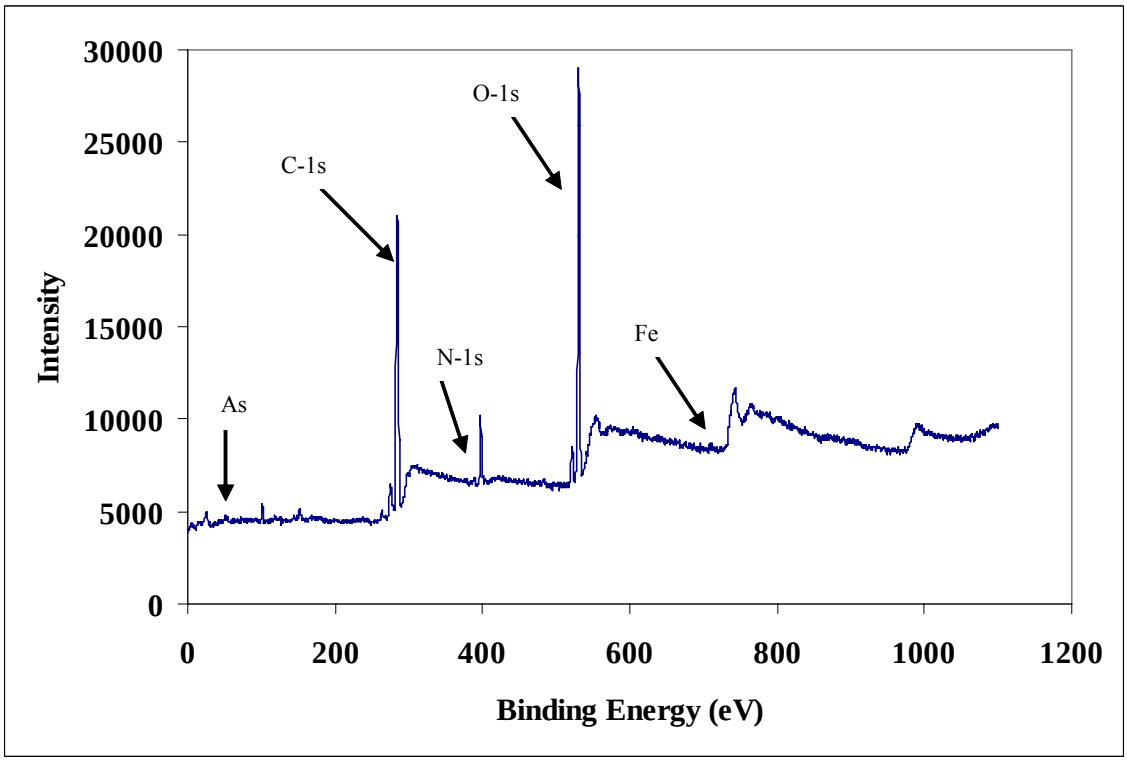

Fig. 2 XPS spectrum of arsenite uptake on iron-chitosan bead

Table 1 Atomic concentrations of C, N, O and Fe on pure iron-chitosan (BE: Binding Energy)

Sample	C		N		O		Fe	
CFeN	BE (eV)	Atomic Conc. (%)	BE (eV)	Atomic Conc. (%)	BE (eV)	Atomic Conc. (%)	BE (eV)	Atomic Conc. (%)
	283.0	77.04	398.0	2.62	530.5	14.33	711.0	0.36

Table 2 Atomic concentrations of As (III), C, N, O and Fe on pure iron-chitosan as obtained from XPS data.

Sample	C		N		O		Fe		As	
CFeN	BE (eV)	Atomic Conc. (%)	BE (eV)	Atomic Conc. (%)	BE (eV)	Atomic Conc. (%)	BE (eV)	Atomic Conc. (%)	BE (eV)	Atomic Conc. (%)
	284.0	71.05	401.5	1.96	530.5	14.50	715.0	0.38	42.50	0.10

Task 2. Optimization of the Sportion under Different Environmental Conditions.

Kinetics of Adsorption

Kinetics of the arsenic(III) removal by iron-chitosan has been conducted at various concentrations. The adsorption studies were performed at room temperature (25°C). The pH of the solutions was maintained at 9.0 because maximum removal arsenic was obtained near pH = 9. The adsorbent loading for initial concentrations of 306, 584, and 994 µg/L was 0.2 g/L. A desired quantity of the adsorbent iron coated chitosan (20 mg) was placed in a separate conical flasks with pH-adjusted As(III) solution. The conical flasks were covered with parafilm and placed on shaker, and these solutions were then removed periodically, and filtered. The amount of As(III) adsorbed by the adsorbent was calculated by analyzing the filtrate solution.

Results from the kinetic batch experiments presented in Figure 3 suggested that adsorption capacity at equilibrium increases from 1.51 to 4.60 mg/g with an increase in the initial arsenic(III) concentration from 306 to 994 µg/L. Above 60% of the arsenic has been adsorbed by the iron-chitosan within 30 min and it takes about 2 hours to reach the equilibrium concentration. At the beginning, adsorption rate was fast, since there was more number of active sites to adsorb the arsenic.

It has been observed that the sorption rate of As(V) and As(III) on minerals was initially rapid and was followed by slow phase (Arai et al. 2004). Fuller et al. (1993) reported that As(V) adsorption on synthesized ferrihydrite had a rapid initial phase (<5 min) and adsorption continued for 182 h. Fuller et al. (1993) proposed that rate limiting As(V) adsorption step was controlled by slow

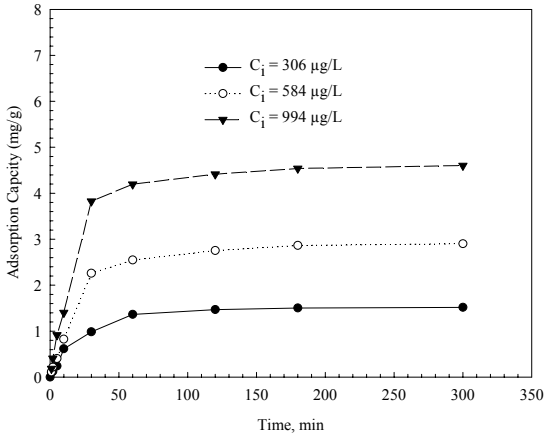

Fig. 3 Rate of adsorption at different initial Concentrations, pH = 9; T=25 °C.

diffusion to adsorption sites within aggregates of ferrihydrite crystalline. Raven et al. (1997) studied the kinetics of As(V) and As(III) adsorption on ferrihydrite from 5 min to 96 h and it was found that most adsorption occurred within the first 2 h. In the study of As(III) adsorption kinetics (0.5 – 24 h) on surface and subsurface of soils, Elkhatib et al. (1984) concluded that the initial reaction was rapid, with more than 50% of As(III) adsorbed in soils in the first 0.5 h.

In order to determine reaction rate constants of arsenic adsorption onto iron coated chitosan two different kinetic models were used, including pseudo-first-order model, and pseudo-second-order model. Kinetics of a pseudo-first-order model can be expressed as (Sarkar and Chatoraj, 1993):

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (1)$$

Where, k_1 is the rate constant of pseudo-first-order adsorption, q_t (mg/g) is the amount of As(III) adsorbed at time t, and q_e is the amount of adsorption at equilibrium. After integration and applying the initial conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, then Equation (1) becomes

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (2)$$

k_1 and q_e can be obtained from the slope and intercept of the kinetics of the first order plot.

A pseudo-second-order equation can be represented as follows (Ho and Mckay 1999)

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (3)$$

Where, k_2 is the rate constant of pseudo-second-order reaction adsorption. Integrating the Equation (3) and applying the initial conditions, we get

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \qquad (4)$$

k_2 and q_e can be obtained from the intercept and slope of the plot of (t/q_t) vs. t.

The kinetic study results are shown in the Figure 4 and 5. Table 3 lists the regression coefficients for the linear plots from the pseudo-first-order and pseudo-second-order equations. It can be seen that R^2 values for pseudo-second-order are greater than those obtained for the pseudo-first-order. This suggested that the arsenite adsorption onto iron coated chitosan may follow the pseudo-second-order reaction. Onyango et al. (2003) investigated the arsenic adsorption kinetics on the surface of chemically modified zeolite. It was concluded that sorption onto the active sites was consistent with a pseudo-second-order mechanism. Arsenite [As(III)] adsorption onto granular ferric hydroxide (GFH) was also analyzed by Thirunavukkarasu et al. (2003) and it was reported that the most of As(III) adsorption onto GFH occurred at pH 7.6, with 68% of As(III) removed within 1 h and 97% removed at the equilibrium time of 6 h and kinetic data were fitted to the pseudo-second-order reaction rate model.

The second order rate constants (k_2), and equilibrium adsorption capacities (q_e) were calculated from the Figures 4 and 5 given in the Table 3. It can be noticed that the rate constant was decreased from 3.194×10^{-2} to 1.151×10^{2} g mg^{-1} min^{-1} as the initial

concentration increased from 306 to 994 µg/L, where as the initial rate ($k_2 q_e^2$) was increased from 5.206×10^{-2} to 5.674×10^{-2} with increasing initial As(III) concentration.

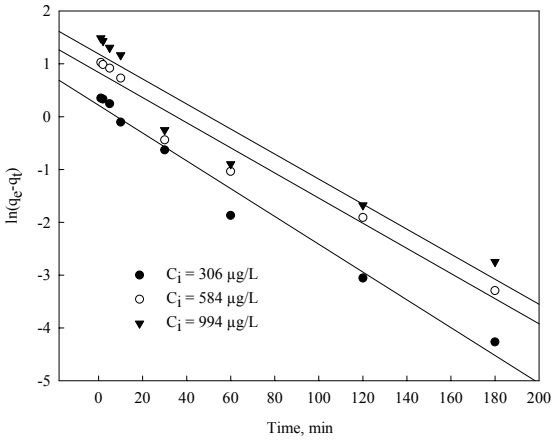

Fig.4 Kinetics of a pseudo-first-order model. pH = 9; Temperature 25 °C

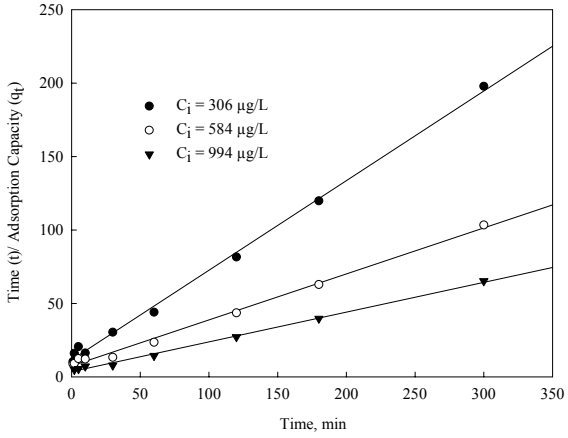

Fig.5 Kinetics of a pseudo-second-order model. pH = 9; Temperature 25 °C

Table 3 Reaction rate constants

Initial Concen-tration (µg/L)	pseudo-first-order				pseudo-second-order			
	$k_1\times10^2$ (min^{-1})	R_1^2	$q_{e,\exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	$k_2\times10^2$ (g mg^{-1} min^{-1})	R_2^2	$q_{e,\exp}$ (mg/g)	$q_{e,cal}$ (mg/g)
306	2.63	0.98	1.51	1.24	3.19	0.99	1.51	1.63
584	2.38	0.96	2.90	2.30	1.31	0.99	2.90	3.19
994	2.37	0.93	4.60	3.26	1.15	0.99	4.60	4.93

Effect of Anions on Arsenic Removal

Several anionic components might exist in groundwater sources which could compete with arsenic for the available adsorption sites (Katsoyiannis et al., 2002). Among the major co-existing anionic components, sulfate, phosphate, silicate, carbonate, and chloride are usually present in groundwater streams possibly inhibiting arsenic removal. In this study, effects of anions are coupled with pH, since anionic hydroxyl group is known to interact strongly with (hydr) - oxide surfaces and also effects acid/base speciation of other anions (Gu et al., 2005). Different concentrations (50 - 100 mg/L) of anions (SO_4^{2-}, PO_4^{3-}, SiO_3^{2-}) were selected on the basis of the concentrations of anions in natural water. In order to investigate the effect of these anions on As (V) and As (III) removal, arsenic solutions were spiked with sulfates, phosphates, silicates and assessed their effects on the arsenate and arsenite removal

under various pH. Arsenic concentration was set at 1000 μg/L. The results obtained are presented in Figures 6 and 7.

Figures 6 and 7 show that SO_4^{2-} did not significantly affect arsenate and arsenite removal from DI water. It can be noticed that in the presence of sulfates, the decrease in arsenate removal percentage was found to be higher at pH >9.0, when compared to arsenite, which was found to be quite moderate at the same pH (Fig. 6 and Fig. 7) and the results were comparable to the solution (no anions supplemented). Furthermore, it can be seen that the presence of phosphate and silicate decreased As (III) removal slightly in the pH range from 7.72 to 9.15. But with further increase in pH, a major decrease on arsenite removal was observed i.e., at pH > 9.2(Fig.7). At pH >9.87 only 25% of arsenite could be adsorbed in the presence of phosphate and silicate. Regarding As (V) removal, a slight decrease was observed in the pH range from 7.2 to 8.8 in the presence of phosphate and silicate. But with further increase in pH, a considerable decrease on arsenate removal was observed. At pH>9.8 only 19% of arsenate could be adsorbed in the presence of phosphate and silicate (Fig.6). These indicate that phosphate and silicate compete with hydroxyl group for the iron surface in the alkaline solution and subsequently decrease arsenate adsorption.

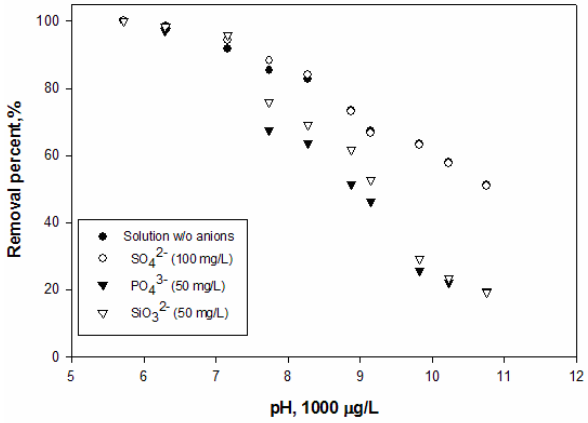

Fig. 6 Effect of anions on arsenate removal under various pH conditions. Initial As (V) concentration is 1.00 mg/L (Ionic strength controlled by 0.05 M Nail)

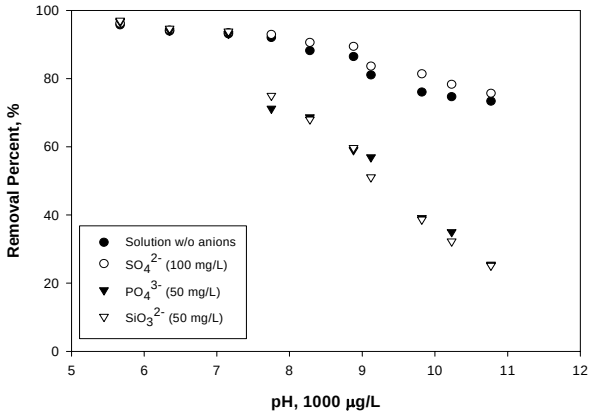

Fig. 7 Effect of anions on arsenate removal under various pH conditions. Initial As (III) concentration is 1.00 mg/L (Ionic strength controlled by 0.05 M Nail)

The presence of the anions such as sulfates, phosphates, silicates in source water has been reported to interfere with arsenic removal (Hering et al., 1996; Meng et al., 2000, 2002; Holm, 2002). Genç and Tjell indicated that phosphates and silicates had major effect on arsenic removal than that of sulfates (Genç-Fuhrman et al., 2004). The presence of sulfate in the influent water produces a slight reduction in As (V) removal, while silicate results in a much higher reduction due to competition (Ghosh et al., 1985; Gupta et al., 1978), supporting the results obtained in this study. Dissolved silicate is usually found in much higher concentrations than phosphate, and can interfere with removal of both arsenate and arsenite (Ghurye et al., 1999). Both arsenite and arsenate have a high affinity for Fe-oxides (Goldberg and Johnston, 2001; Smedley and Kinniburg, 2002), suggesting that the presence of Fe (III) could enhance the sorption properties of the adsorbent. Phosphates are adsorbed on iron hydroxides through the formation of surface complexes with the hydroxyl groups (Meng et al., 2001), decreasing greatly the efficiency of arsenic removal. Gu and Fang's study (2005) on adsorption onto granulated activated carbon indicated that phosphates and silicates show

great decrease in the removal of arsenic at pH >9.0 when compared to the removal of arsenic in the presence of sulfates. This is consistent with the results obtained in this study.

Adsorption Isotherms

Adsorption isotherms describing the distribution between aqueous and adsorbed phases for As(III) at different initial concentrations and different pH of the solutions have been shown in the Figures 8 and 9. It can be observed that maximum adsorption capacity increased from 1.95 mg/g to 5.97 mg/g and from 1.97 mg/g to 6.48 mg/g as the initial concentration of arsenic increased from 0.3 mg/L to 1 mg/L for pH = 7 and pH = 8 respectively. As the pH of the solution reduced from 8 to 7 the adsorption capacity was reduced about 1-8 %. Because as the solution becomes basic from neutral medium initially the adsorption efficiency was increased slightly (from pH effect plot), therefore when the initial concentration increased the maximum adsorption capacity was reduced for pH reducing from 8 to 7. Ferguson and Anderson (1974) also reported that arsenite adsorption on iron oxide decreased with decrease in the pH from 8 to 6.

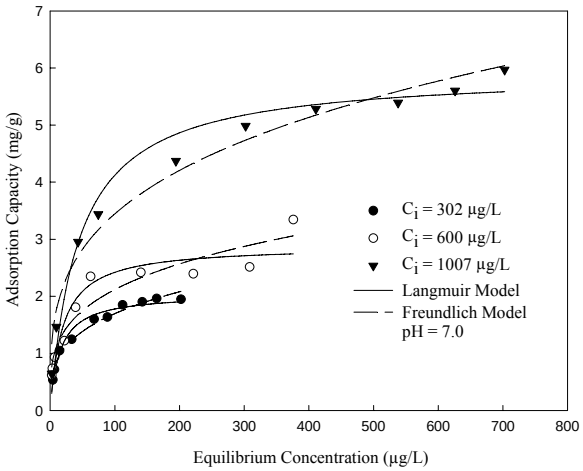

Fig. 8 Adsorption isotherms at different initial concentrations, pH = 7.0
Experimental data fitted to the Freundlich model (dash lines) and Longmuir model (solid lines).

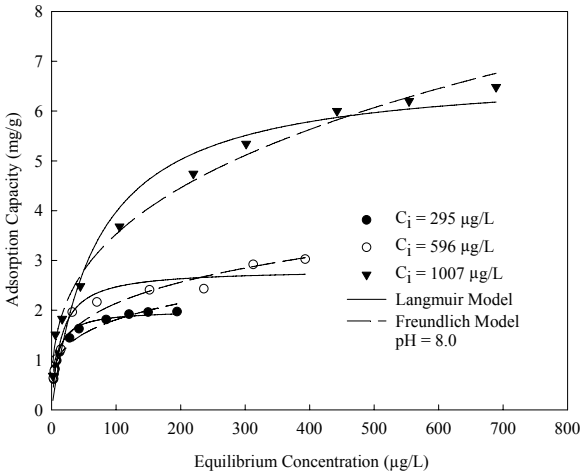

Fig. 9 Adsorption isotherms at different initial concentrations, pH = 8.0
Experimental data fitted to the Freundlich model (dash lines) and Longmuir model (solid lines).

An equilibrium model of either the Freundlich or Langmuir type is commonly utilized to describe such adsorption phenomenon. The Freundlich isotherm model is represented mathematically as follows:

$$q = k_f C^{1/n}$$

Where, q is the amount of As(III) adsorbed per unit mass of adsorbent (mg/g), C is the concentration of As(III) in solution (µg/L), k_f and $1/n$ are parameters of Freundlich isotherm, denote the distribution coefficient (L/g) and intensity of adsorption respectively. Langmuir equation is another widely used equilibrium adsorption model. It has the advantage of providing a maximum adsorption capacity $q_{\max}$ (mg/g) that can be correlated to adsorption properties. Longmuir model can be represented as:

$$q = q_{\max} \frac{K_L C}{1 + K_L C}$$

Where, q is the amount of As(III) adsorbed per unit mass of adsorbent (mg/g), C is the concentration of As(III) in solution (μg/L). $q_{\max}$ and K_L are Longmuir constants representing maximum adsorption capacity (mg/g) and binding energy (L/mg).

In order to obtain isotherm parameters, Freundlich model and Langmuir model were used to fit the experimental data using the non-linear regression software. It was found that both Freundlich and Langmuir equations could fit the As(III) adsorption shown in Figures 8 and 9. However, Freundlich model had little better agreement with experimental data, as indicated by the higher regression co-efficient values in Table 4 when compared to the Langmuir model. Freundlich parameter adsorption intensity ($1/n$) values were found to be varying from 0.24 to 0.34 for different concentrations at different pHs.

Table 4 Adsorption isotherm parameters

Initial Concentration (μg/L)	pH	Freundlich parameters			Longmuir constants		
		k_f (L/g)	$1/n$	r_1^2	$q_{\max}$ (mg/g)	K_L (L mg^{-1})	r_2^2
295	7.0	0.44	0.27	0.98	2.05	0.07	0.97
596	7.0	0.59	0.28	0.92	2.88	0.05	0.89
1007	7.0	0.91	0.29	0.97	5.90	0.02	0.97
295	8.0	0.59	0.24	0.96	2.01	0.12	0.99
600	8.0	0.64	0.26	0.95	2.82	0.07	0.95
1007	8.0	0.75	0.33	0.99	6.82	0.01	0.95

It can be observed from the Freundlich parameters that adsorption intensity ($1/n$) and distribution coefficient (k_f) were increased as the initial concentration of arsenic increased in the solution. This illustrates the dependence of the adsorption on initial concentration. Low $1/n$ values (<1) from the Freundlich isotherm suggested that any large change in the equilibrium concentration of arsenic would not result in a significant change in amount of arsenic adsorbed. Selim and Zhang (2005) reported that adsorption isotherms for As(V) by different soils were better fit to the Freundlich model and adsorption intensity values for As(V) by different soils were found to be 0.270, 0.340, and 0.284. Similarly low $1/n$ values for As(V) adsorption have reported by others (Buchter et al., 1989; Manning et al., 1997). Other similar results were also obtained from the arsenic adsorption onto granular ferric hydroxide by Thirunavukkarasu et al. (2003).

Langmuir adsorption maxima $q_{\max}$ increased significantly as the initial arsenic concentration increased. Where as the Langmuir coefficient K_L exhibited a decreasing

value as the initial concentration increased, which indicates that binding energy of As(III) to the adsorbent is decreasing as the initial concentration increases. A study on removal of arsenic by iron coated GAC by Gu et al. (2005) reported similar results of decreasing binding energy as the initial concentration of arsenic increasing.

Column Study

Column tests were conducted to investigate the use of iron coated chitosan as a low-cost treatment technology for arsenic removal. Experiments were conducted with 12-mm-ID glass column at a flow rate of 25 ml/h (empty bed contact time 2.5 min) with an initial arsenic concentration of 308 μg/L. To determine the breakthrough curve, 1.5 g adsorbent was packed in the column as fixed bed. Then arsenic solution was passed through the fixed bed and effluent solution was analyzed for arsenic concentration. The result of breakthrough curve was given in Figure 10. It can be seen that the break point obtained after 768 bed volumes and adsorbent was exhausted at 1400 bed volumes. Gu et al. (2005) examined the arsenic breakthrough behaviors for an As-GAC sample prepared from Dacro 20×40 LI with an initial concentration of 56.1 μg/L As(III). The duration of column studies ranged from 45 to 70 days with an empty bed contact time of 5 min. The results demonstrated that the adsorbent could effectively remove the arsenic from groundwater in the column setups. Both As(III) and As(V) were in the system, the column could treat over 4500 bed volumes of water prior to breakthrough.

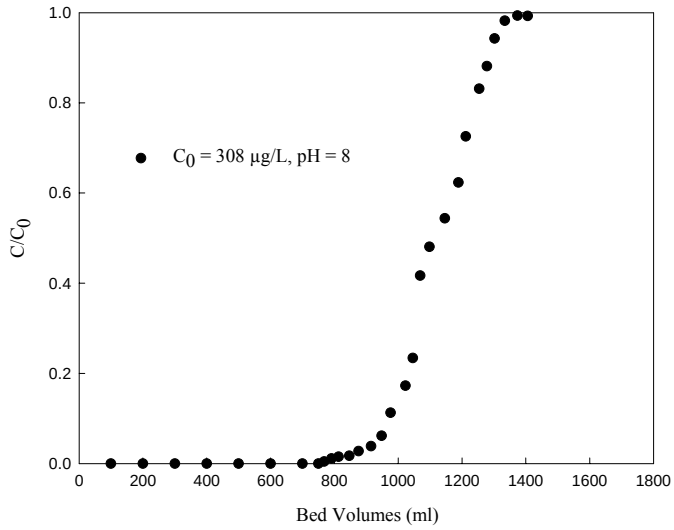

Figure 10 Column study

SUMMARY

In the past six months, all components in tasks 1 to 3 are finished. Adsorption experiments demonstrated that iron-chitosan can be used to remove arsenic from aqueous solution. The adsorption isotherm fitted Freundlich model well and the maximum adsorption removal efficiency was observed at pH = 9.1. Kinetic batch experiments results indicated that about 60% of the arsenic was adsorbed by the iron-chitosan within the first 30 min and pseudo-second-order model fitted the experimental data well. Effect of anions on arsenic removal

studies showed that competition in multi-sorbate systems could significantly restrain arsenic adsorption, especially if silicate ion is present. Sulfate has only a minimal effect, while phosphate reduces adsorption considerably at pH values greater than 7 where anion adsorption sites are limited. Column studies showed that the breakthrough point was at 768 empty bed volumes (EBV) when flow rate was 25 ml/hr.

FUTURE WORK

In the next reporting period, the project will be finished. The efforts will include: (1) Write final report (2) Prepare paper for publishing.

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PUBLICATIONS/PRESENTATIONS

None in this period.

Appendix 25: Determination of Factors Affecting the Separation of Potentially Hazardous Trace Elements and their Behavior in Coal Tailings Impoundments (KY005)

TECHNICAL PROGRESS REPORT

Contract Title and Number:	Period of Performance:
Crosscutting Technology Development at the Center for Advanced Separation Technologies (DE-FC26-02NT41607)	Starting Date: 6/1/2005 Ending Date: 10/31/2006

Sub-Recipient Project Title:	Report Information:
Determination of Factors Affecting the Separation of Potentially Hazardous Trace Elements and their Behavior in Coal Tailings Impoundments	Type: Semi-Annual Number: 2 Period: 4/1/06-9/30/06 Date: 09/30/06 Code: KY005-R02
Principal Investigators:	
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Subcontractor Address:	Subcontractor Information:
No subcontracts issued.	Phone: Fax: E-Mail:

ABSTRACT

The project made significant progress in the latest reporting period. Almost all of the analyses to be performed on the run-of-mine coal and various clean and reject products from the Peabody Gateway Coal preparation plant in Coulterville, Illinois, have been completed, except for the mineralogical analysis by CCSEM. Such analyses include ultimate and proximate analyses, forms of sulfur, ash chemistry (major elements) by XRF, trace elements by ICP-MS, and mercury by CVAAS. In addition, elemental speciation data were obtained using XAFS spectroscopy for As, Cr, S, Se, Pb and Zn and Mossbauer spectroscopy for iron. As the data accumulate, we are beginning to obtain valuable insights into why selected hazardous trace element behave the way they do in gravity separation processes for coal cleaning. For example, some excellent XAFS data were obtained for Cr showing that much of the Cr in this particular Illinois coal is associated with illite, which accounts for its good separation. This result contrasts with a previous study on a different Illinois basin coal that showed that Cr is largely associated with the organic components and separates poorly.

The four coal fractions were also evaluated for element leachabilty using the TCLP protocol and XAFS and Mossbauer techniques were used to examine changes in the forms-of-occurrence of arsenic and iron. As a result of the negative results from the TCLP method, we have designed and constructed equipment for longer term leaching tests on coal rejects.

INTRODUCTION

Background

The major goal of separation technology is to increase the yield of valuable product by separating it from undesirable waste components. In the coal separation industry that serves the electrical power generation industry, the specific goal is to separate the incombustible mineral matter from the combustible macerals in order to develop a clean-coal product that has a higher calorific value and generates less combustion wastes and emissions. Such coal cleaning is especially valuable for coals from the bituminous coal regions of the eastern United States, since the mineralogy of the coals from these regions is generally dominated by quartz, clays and pyrite, which are minerals in coal that can be separated efficiently by conventional and/or advanced coal-cleaning methods. Such cleaning also removes certain trace elements designated as hazardous air pollutants (HAPs) by the 1990 Clean Air Act Amendments (CAAA). However, such HAP elements are then often concentrated in coal tailings and may become of concern to the 1976 Resource Conservation and Recovery Act (RCRA) during disposal of the mineral-rich tailings. The partitioning of a trace element between clean product and tailings is determined by the mineral phase in which the element occurs, its valence and magnetic states, and association with major inorganic or carbonaceous components of the coal. These mode-of-occurrence factors have only rarely been determined with respect to trace elements in coal cleaning operations and, as far as we can tell, never with respect to their behavior in coal tailings disposal options.

Objective and Approach

The principal objective of this investigation is to determine why some hazardous air pollutant (HAP) elements separate well and others poorly during various coal cleaning processes. To address this issue, basic information regarding the occurrence of trace elements and minerals in coal and their behavior in coal cleaning processes will be obtained using a variety of techniques that enable us to determine the mineralogy of the coal and mode of occurrence of specific elements. Such techniques include computer-controlled scanning electron microscopy (CCSEM) to determine the mineralogy and mineral size distributions in both clean and tailings fractions and X-ray absorption fine structure (XAFS) spectroscopy to obtain direct data on the speciation of trace elements of interest. The secondary objective is to investigate and interpret the behavior of the HAP elements in laboratory simulations of the disposal of tailings in ponds using similar methods.

PROJECT TASKS

During the latest reporting period, we have concentrated on obtaining and evaluating analytical data for the four fractions of the Illinois coal obtained from the Peabody Gateway Preparation Plant, Illinois. A minor problem with the preparation of epoxy mounts, however, has prevented us from obtaining mineralogical data by CCSEM. Owing to negative results from the TCLP leaching protocol, new batch leaching equipment has been constructed for long-term testing of the leachability of trace elements from the tailings fractions and is currently undergoing final testing.

Task 1 – Sample Preparation: Nothing to report on this task.

Task 2 – Analysis Methods: The following analyses were conducted and completed on each of the four coal fractions during the reporting period:

A. Ultimate, proximate, forms of sulfur, heating value
B. XRF for major elements on 500^{o}C ash prepared from each fraction
C. Trace element analyses by ICP-MS and individual analyses for Hg
D. Fe speciation and oxidation state by Mossbauer spectroscopy
E. Speciation of As, Cr, Pb, Se, S, and Zn by XAFS spectroscopy.
F. TCLP testing of the four fractions
G. Mossbauer analysis of Fe and XAFS analysis of As in the TCLP leached residues.

We were hoping also to have complete information on the mineral matter and mineral size distributions by CCSEM by now, but this has not yet proven possible because of a problem preparing polished epoxy mounts of aliquots of the coal fractions. Our efforts to date result in the formation of fine bubbles in the epoxy mount which confound the analysis in the CCSEM. We have tried a number of different epoxies and heating the sample mount as the epoxy components react with no success. Other avenues that we are exploring include pre-drying of the coal fractions and preparation in vacuo in order to circumvent this problem.

All four samples were subjected to conventional TCLP analysis at American Testing Co. of Pennsylvania. The results for the leachability of As, Ba, Cd, Cr, Pb, Se, Ag, and Hg were negative for all four fractions and changes in the As and Fe speciation sought for by XAFS and Mossbauer spectroscopies were insignificant. These results convinced us of the need to design and build equipment for longer-term testing of element leachabilities from the tailings fractions. The testing method that we are developing is a variation of ASTM standard method D-5744 for leaching of solid waste materials [1].

Table 1: Ultimate Analysis of Coal Fractions

Sample (ID)	%Ash	%Moisture	%C	%H	%N	%S	%O
RB Feed (FEE)	27.66	5.15	52.52	4.1	0.98	4.09	10.65
RB Reject (RBR)	76.47	5.53	10.78	1.58	0.25	3.54	7.38
Clean Coal (CLN)	9.16	4.64	67.54	5.14	1.25	3.3	13.61
Plant Reject (PRJ)	73.16	3.21	13.85	1.5	0.34	5.14	6.01

Task 3 – Results: Results of ultimate analysis are summarized in Table 1. Except possibly for oxygen, these values appear reasonable. The values for wt% S are all relatively high and indicate a large organic sulfur content for the coal; this was confirmed by forms of sulfur analyses. Data from iron Mossbauer spectroscopy and forms of sulfur analysis (Table 2) indicate that the pyrite content of the reject from the rotary breaker (RBR) is significantly higher than that of the reject from the heavy media cyclones and spiral separators in the plant (PRJ). Conversely, data from chemical analyses of the ash (not shown) indicate that the PRJ is richer in clays than the RBR. Hence, these differences in the reject fractions will be useful for distinguishing between elements that are more strongly associated with pyrite or clay

minerals. Also shown in Table 2 are data for the Hg content of the coal fractions. It can be seen that the mercury contents correlate reasonably well with the measures of pyritic sulfur.

Table 2: Results from forms of sulfur analyses, pyritic sulfur by Mossbauer spectroscopy, and from CVAAS for Hg

	Mossbauer	Forms of Sulfur			
Sample ID	Wt% S pyritic	Wt% S pyritic	Wt% S sulfate	Wt% S org S	Mercury ppm
RB Feed	2.20	1.98	0.11	2.00	0.08
RB Reject	3.59	2.88	0.1	0.56	0.09
Clean Coal	1.05	0.86	0.11	2.33	0.06
Plant Reject	4.46	4.67	0.19	0.28	0.18

Speciation data for a number of HAPs elements have been obtained for the four coal fractions by X-ray absorption fine structure (XAFS) spectroscopy. As an illustration of the value of such data, we present some details of our findings for chromium. The data on trace element concentrations by ICP-MS (not shown) show that Cr in this Illinois coal is relatively abundant, separates rather efficiently between the clean coal and reject fractions, and correlates reasonably well with wt% ash (Figure 1). The explanation for this behavior is readily apparent from the XAFS spectra of Cr in the coal fractions. We obtained excellent quality XAFS spectral data for this element (Figure 2) and, based on published XAFS data for Cr in minerals in coal [2], we are able to identify that the Cr in the RBR and PRJ fractions is predominantly associated with the clay mineral, illite. A quite different spectrum was obtained for the CLN fraction, indicating that there are two significant forms of Cr present in this coal that are efficiently fractionated by the separation methods. The Cr XANES spectrum of the feed coal (FEE) is intermediate. Further, it can be well simulated by weighted addition of the spectra for the CLN (37%) and PRJ (59%) fractions. A previous investigation [3] of Cr in coal from the Kentucky #9 seam found a much stronger association of Cr with the organic matter in coal and relatively poor separability. The differences between these two coals with respect to Cr emphasize the importance of the form of occurrence for understanding the behavior of elements in separation technologies.

Also, based on the XAFS spectra, we conclude that the Cr is entirely (>95%) present in the Cr^{3+} oxidation state; there is no indication in these spectra of the presence of any of the much more toxic and soluble Cr(VI) oxidation state. Such information for Cr and similar data for other elements will be useful for evaluating the results of the leaching tests to be obtained with the new leaching equipment.

Similar inferences to those described here for Cr have been made for other key elements. The CCSEM mineralogical data, once obtained, should allow us to quantify some of these trends.

FUTURE WORK

Over the next six months, we should complete our analyses of the Illinois coal fractions and be in a position to evaluate the role and importance of the form of occurrence in determining the behavior of key elements in float/sink separation technologies. In addition, long-term

leaching experiments will commence on the two reject fractions to assess the relationship of elemental forms of occurrence to their leachability. We also intend to initiate additional studies with the Illinois coal using different coal separation technologies.

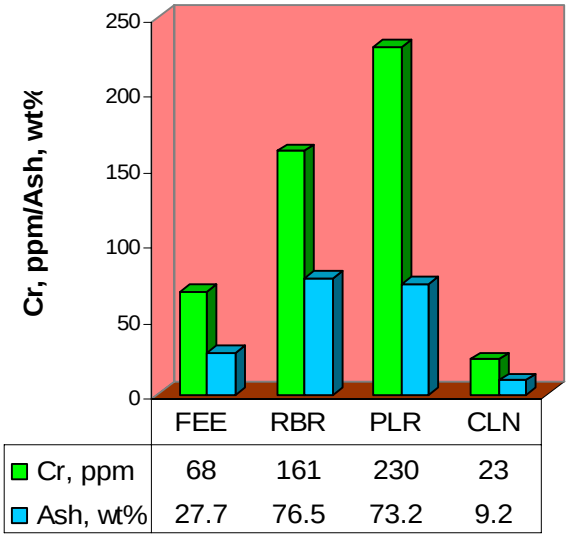

Figure 1: Histogram comparing the Cr and ash contents of the different fractions from the Illinois coal. Note the correlation of wt% ash and ppm Cr across the different fractions.

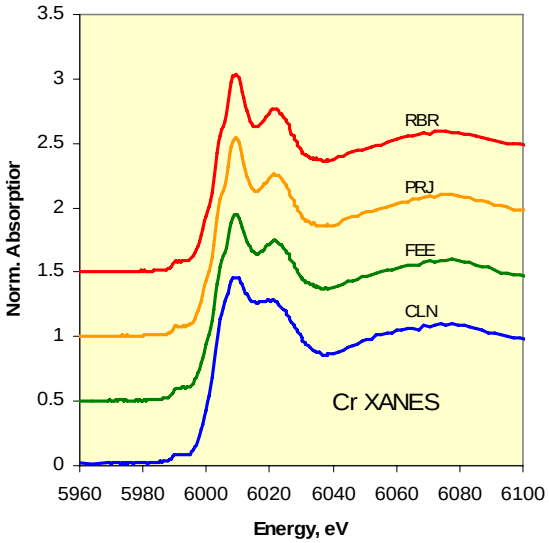

Figure 2: Cr XANES spectra of Illinois coal fractions. The Cr in the two reject fractions, RBR and PRJ, is predominantly present in association with illite, whereas the Cr is associated with macerals in the CLN fraction.

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3. F. E. Huggins, S. Srikantapura, B. K. Parekh, L. Blanchard, and J. D. Robertson, *XANES spectroscopic characterization of selected elements in deep-cleaned fractions of Kentucky #9 coal.* **Energy & Fuels**, 11, 691-701, (1997).

PUBLICATIONS/PRESENTATIONS

None.

Appendix 26: Mercury Reduction From Coal Power Plant Emission Using Functionalized Ordered Mesoporous Carbons (FOMCs) (WV015)

TECHNICAL PROGRESS REPORT

Contract Title and Number:	Period of Performance:
Crosscutting Technology Development at the Center for Advanced Separation Technologies (DE-FC26-02NT41607)	Starting Date: 06/01/2005 Ending Date: 10/31/2007

Sub-Recipient Project Title:	Report Information:
Mercury Reduction From Coal Power Plant Emission Using Functionalized Ordered Mesoporous Carbons (FOMCs)	Type: Semi-Annual Number: 2 Period: 03/1/06-09/30/06 Date: 09/30/06 Code: WV015-R02
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Subcontractor Address: Baolin Deng Department of Civil & Environmental Engineering University of Missouri-Columbia Columbia, MO 65211	Subcontractor Information: Phone: 573-882-0075 Fax: 573-882-4874 E-Mail: DengB@missouri.edu

ABSTRACT

In the previous project period, we established experimental setups and synthesized ordered mesoporous carbon in multi gram quantity needed for the research. During the current project reporting period, effort is devoted to modify the ordered mesoporous carbon with various procedures and characterize the effectiveness of such modifications. The modifications include adding amine groups and sulfur to the surface of the ordered mesoporous carbons (OMCs). Sample characterizations with FTIR, XRD, and TEM have been applied, which have confirmed the success of the functionalization procedures. Some preliminary tests are conducted with activated carbon to develop modification procedures for OMC.

INTRODUCTION

Background

Technologies for mercury control from coal-fired power plants (CFPPs) have been well explored. Activated carbon adsorption has been demonstrated to be able to control mercury emissions. These adsorption processes can be accomplished in two different ways: powdered activated carbon (PAC) injection and fixed-bed granular activated carbon (GAC)

adsorption. PAC injection involves the injection of PAC directly into the plant's flue gas stream where it adsorbs gas-phase mercury and is collected in downstream particulate control devices, such as fabric filters. In the fixed-bed GAC adsorption situations, GAC is placed downstream of the flue gas desulfurization (FGD) units and particulate collectors, serving as the final treatment process before the flue gas is discharged into the atmosphere. The regular activated carbons with large fraction of micropores (< 2 nm) are not suitable for large-sized contaminants and their applications can be limited by slow diffusion kinetics, especially in the high particulate environment. Another study demonstrated that regular activated carbon showed little adsorptive capacity for elemental mercury when temperature is over 90° because of the physical adsorption mechanism of Hg onto virgin GAC (Vidic, et al 1996).

Ordered mesoporous carbons (OMCs) have attracted much attention in recent years because OMCs could be widely utilized in industries as catalyst supports and gas separation media, etc. There is also a great potential to use OMCs for environmental improvement, including the removal of inorganic and organic contaminants from liquid and gas phases. Although functionalized regular thermal activated carbons have been reported using sulfur to remove mercury from flue gas of CFPPs, no research work has been started on functionalized OMCs. The investigators believe that functionalized OMCs would have great potential in the elemental mercury removal from flue gas because of their desirable properties, such as high surface area, controlled pore size, and elemental mercury reactive functional groups.

Objective and Approach

The objective of this project is to develop and evaluate a novel method for removing elemental mercury by using functionalized ordered mesoporous carbons (FOMCs). Ordered mesoporous carbons (OMCs) will be synthesized under defined conditions and their structure will be optimized according to their capability toward mercury removal. Then, OMCs will be functionalized by sulfur and other chemicals to enhance Hg uptake. Three research tasks are proposed: (i) Synthesize high surface area ordered mesoporous carbons (OMCs); (ii) Functionalize the OMCs with different chemicals to enhance Hg uptake; and (iii) Optimize conditions for mercury removal. Task 1 was essentially completed as reported in the previous project period. The current project period has focused on functionalizing the OMCs and assessing the effectiveness of the modifications. Further work will continue on the surface modification and establish an experimental system capable of assessing elemental mercury removal efficiency.

PROJECT TASKS

This period has focused on Task 2 - Functionalize the OMCs with different chemicals to enhance Hg uptake. Three procedures are conducted for adding different functional groups onto activated carbon or OMC. Activated carbon is used in some experiments as preliminary materials for procedure development.

Procedure 1: Addition of amine group onto the activated carbon surfaces

This procedure is adapted from the work by Yantasee et al. (2004) as illustrated by the reactive scheme presented in Figure 1.

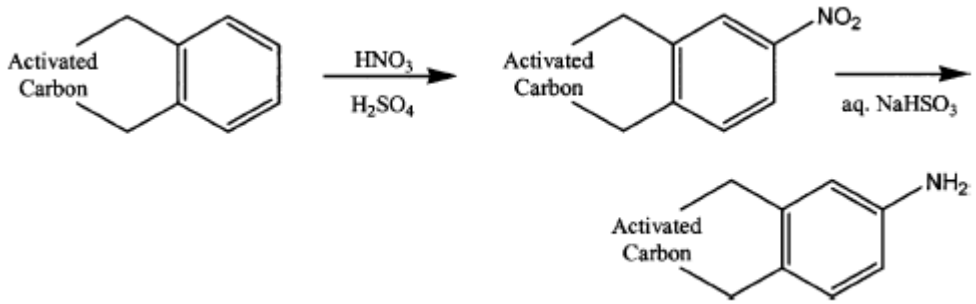

Figure 1. A two-step process for functionalization of amine group onto activated carbon (Yantasee et al., 2004).

This is a two step process. The first step involves an electrophilic substitution for the nitration of activated carbon. At room temperature, Twenty-five (250 mL of concentrated sulfuric acid (18 M) was added slowly to 25 mL of concentrated (15.7 M) nitric acid (HNO_3). Then, a 4.485 g of as-received activated carbon was slowly added to the acid mixture and stirred for 50 min. The mixture was filtered and washed with deionized water and subsequently with ethanol. The filtrate was then air-dried at ambient temperature. The resulting product from the first step was nitrobenzene. The second step is the conversion of nitroarene to aniline. A 2.53 g of treated activated carbon, 25 mL of water, 10 mL of concentrated ammonium hydroxide, and a stir bar were placed in a 250 mL round-bottom flask and stirred for 30 min. A 25.5 g of sodium hydrosulfite ($Na_2S_2O_3$) was added to this solution slowly and allowed to stir overnight at room temperature. A reflux condenser was fitted on the flask to avoid solvent evaporation due to the increase in the solution temperature. A 10 mL of 17.5 M glacial acetic acid was diluted in 100 mL of water and was then added to the solution and stirred for 5 h at reflux (100°C). The solution was then cooled to room temperature, filtered, washed with a copious amount of water, followed by ethanol, and finally air-dried.

It is important to verify whether the functionalization process is successful. Figure 2 is the FTIR spectra of the functionalized activated carbon (blue) as compared with the un-treated sample (red). Comparing their patterns, after the functionalization with amine, there is a new peak, it is probably amine group.

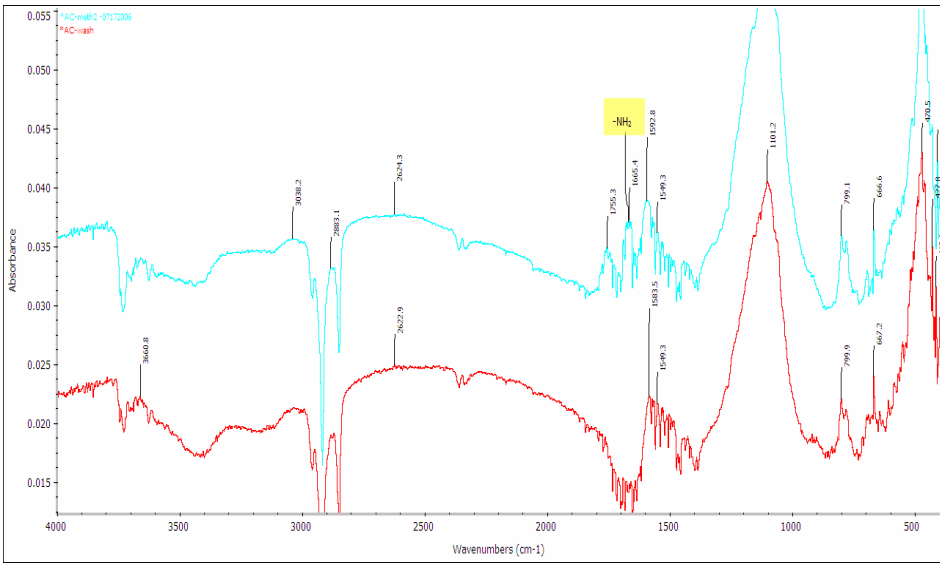

Figure 2. FTIR spectra of the functionalized activated carbon (blue) and un-treated activated carbon (red).

Procedure 2: Functionalization of OMC surfaces with modification

There is no reported procedure for surface functionalization of OMC with amine group, so a procedure is developed based on some studies by Jarrais et al (2005) and Silva et al. (2002) (Figure 3). It involves: (1) OMC oxidation: a 2.5 g of OMC was slowly added to 25 mL of concentrated nitric acid (HNO_3) with heating, and stirred for 120 min. The mixture was filtered and washed with deionized (DI) water, then air-dried at 40°C. (2) Reaction with thionyl chloride: The treated OMC (B1) was refluxed in 5% $SOCl_2$ in dry toluene solution at 70°C for 4 hours, then filtered and extensively washed with toluene, dried in an oven at 40°C for overnight under vacuum. (3) Functionalisation of OMC: the treated OMC (B2) was refluxed with a solution containing amine group compound bis(3-aminopropyl)amine in 40 mL of dry toluene for 4 h, then filtered and extensively washed with toluene. The products were also extracted for 2 h with toluene and dried in an oven at 150 °C for 13 h under vacuum (B3).

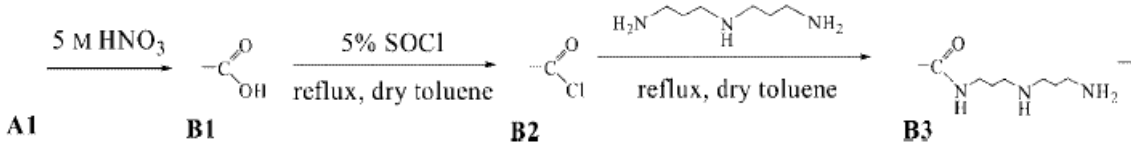

Figure 3. Procedure for functionalization of OMC surfaces (Jarrais et al., 2005)

FTIR spectra of the functionalized OMC (red) and original OMC (purple) are shown in Figure 4. After the functionalization there are two new peaks that are assigned to amine groups.

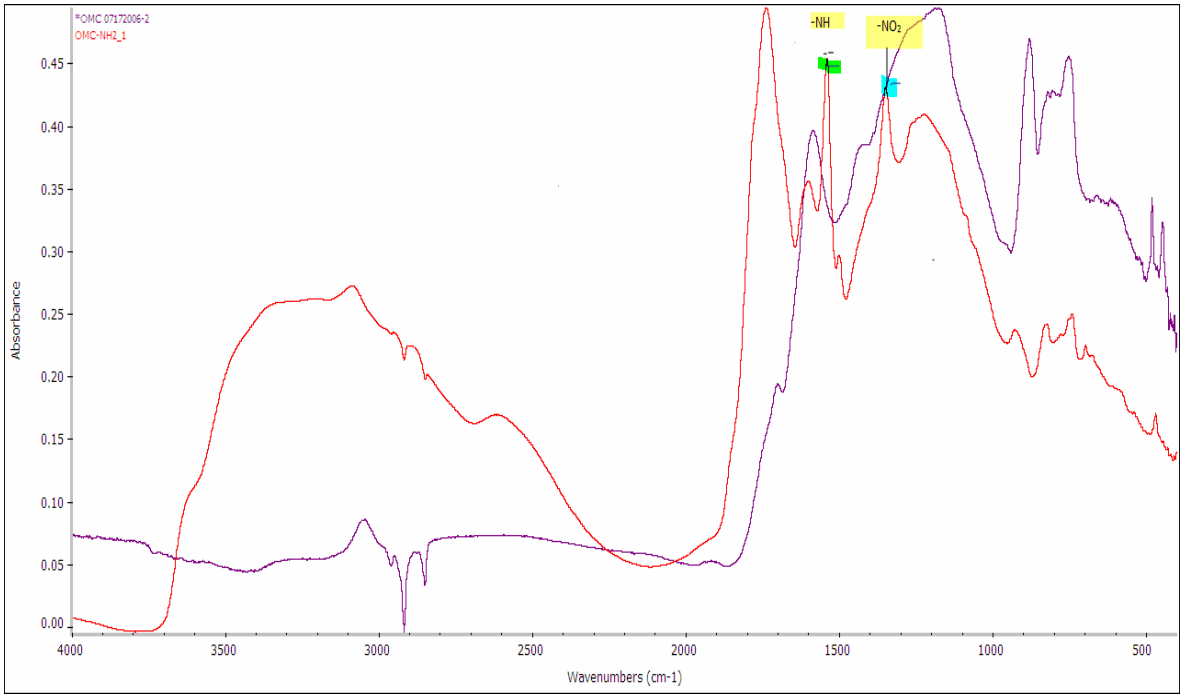

Figure 4. FTIR spectra of the functionalized OMC (red) and un-treated OMC (purple).

This process has significant modified the mesoporous structure, as indicated by XRD analysis (Figure 5). The original peaks in unmodified OMC have replaced with a single peak. The modification is confirmed by TEM micrographs (Figure 6).

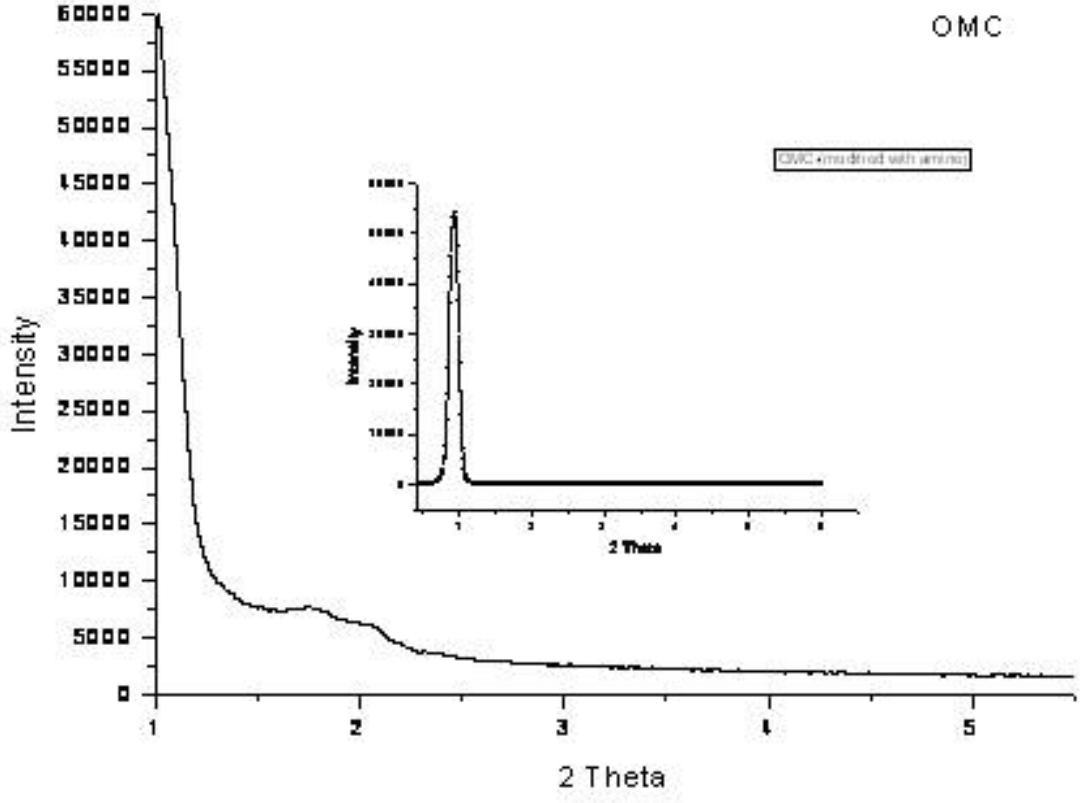

Figure 5. X-ray diffraction patterns of OMC before and after surface functionalization

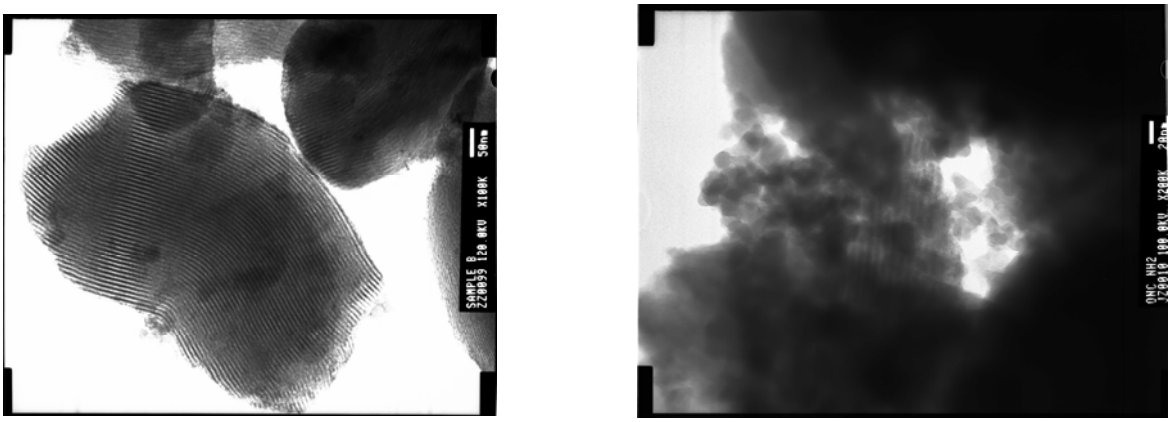

Figure 6. TEM micrographs of OMC before (left) and after (right) functionalization with the procedure 2.

Procedure 3: Functionalization of OMC surfaces with elemental sulfur.

Eight (8) g of OMC and 8 g elemental sulfur were granulated into fine powder and thoroughly mixed. Then the mixture was heated under N_2 flow at a temperature ramp rate of 5°C min^{-1} to 600°C and held for 4 hrs for vulcanization.

SUMMARY

We have tried several approaches to functionalize the surfaces with sulfur and amine functional groups that are expected to have strong affinity for mercury adsorption. Sample characterizations with FTIR, XRD, and TEM have been applied, which have confirmed the success of some functionalization procedures.

FUTURE WORK

We will continue the work with surface functionalization with various functional groups such as amine, sulfur, iodine, and chlorine, and assess how these surface modifications will affect Hg removal efficiency.

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PUBLICATIONS/PRESENTATIONS

(None)

Appendix 27: Removal of Metal Ions from Acid Mine Drainage using a Novel Low-Cost, Low Technology (WV017)

TECHNICAL PROGRESS REPORT

Contract Title and Number:	Period of Performance:
Crosscutting Technology Development at the Center for Advanced Separation Technologies (DE-FC26-02NT41607)	Starting Date: 6/1/2005 Ending Date: 10/31/2007

Sub-Recipient Project Title: Removal of Metal Ions from Acid Mine Drainage using a Novel Low-Cost, Low Technology	Report Information: Type: Semi-Annual Number: 1 Period: 10/1/05-3/31/06 Date: Code: WV017-R01
Principal Investigators: Benjamin Dawson-Andoh	
Contact Address: Division of Forestry West Virginia University Morgantown WV 26506	Contact Information: Phone: (304) 293-3825 x2487 Fax: E-Mail: bdawsona@mail.wvu.edu
Subcontractor Address: Insert address of subcontractor. If none awarded, insert "No subcontracts issued."	Subcontractor Information: Phone: Fax: E-Mail:

ABSTRACT

Preliminary studies to test the proof of concept that wood residues can absorb and remove metal ions from Acid Mine Drainage water is in progress. Delivery and installation of a major piece of analytical equipment, Laser Induced Breakdown spectrometer (LIBs) has been delayed thus slowing down progress of work. Ocean Optics Inc now promises to deliver and install the equipment in November, 2006.

INTRODUCTION

Acid Mine Drainage (AMD) produced by active and dormant coal mines continues to pose a major threat to the environment. One of the goals of the National Energy Policy developed by President Bush in 2001 is "to ensure the steady supply of affordable energy in

environmentally responsible and sustaining manner." Current technologies employed to remove toxic environmental polluting metals from AMD are expensive and economically challenging to the Coal Mining Industry. The work proposed here seeks to evaluate a low-cost, low technology that employs renewable biomaterials: wood and fungal biomass, to remove toxic metals that occur in AMD from solutions. Additionally, the proposed work also seeks to determine the recovery potential of toxic metals from the biomaterials and the regeneration and re-use of the biomaterials. West Virginia is one of the premier hardwood States in the US and tremendous amount of wood biomass is available as residue. The proposed study if successful will provide an avenue for the use of the tremendous wood biomass generated by both the primary and secondary forestry operations in West Virginia.

OBJECTIVES AND APPROACH

The objective of the work proposed here is to compare the relative efficacy of four types of biomaterials: (1) wood residues, (2) chemically modified wood residues, (3) fungal (non-living) biomass, and (5) biologically modified wood biomass containing non-living fungal biomass. Fungal biomass will be immobilized in polyurethane foam. Wood biomass will be evaluated in two forms: particulates (5 mesh size) and mats (low density fiberboards). Since West Virginia is a hardwood (angiosperms) State, this study will focus on two hardwood species: red oak and yellow-poplar. Both wood species commonly occur in West Virginia. Also, two fungal species, *Aspergillus niger* and *Penicillium chyrosgenum* will be investigated.

The efficacy of the biosorptive uptake of each biomaterial will be evaluated by measuring the kinetics of sorption and biosorptive equilibrium isotherm. This study will be carried out at bench scale level. The experimental design will be a factorial:

1. Biomaterials: 2 levels – wood biomass and fungal (non-living) biomass.
2. Modification of biomaterials: 2 levels - chemical and biological.
3. pH: 2 levels – 3 and 5.

PROJECT TASKS

Task 1: Equipment Setup:

We are in the process of purchasing a LIBS system from Ocean Optics, FL. In the meantime, analytical work will be done using inductively coupled plasma emission spectrometry.

Task 2: Experimental

Twenty five gallons of Acid Mine Drainage material was collected from Lick Run, Preston County, WV, on 04/05/2006 and is stored at 3 ^{0}C. Four types of wood residues, oak residue, oak bark, miscellaneous wood mulch and miscellaneous wood residues have been received from Burke-Parsons-Bowlby Corp. 25 g of each wood type, in triplicate, were weighed into 250 ml Erlenmeyer flasks. 200 ml of AMD was added to each flask (wood-AMD ratio, 1:4)

and shaken on a rotary shaker (50 rpm) for 48 hours. Control flasks contained 200 ml AMD and no wood residue. At the end of this period, 10 ml aliquots were taken from each flask and filtered through 0. 22 μm filter. And is currently being analyzed by inductively coupled plasma emission spectrometry

Task 3: Data Analysis

None available now

SUMMARY

A major piece of analytical equipment is expected to be installed in November, 2006 and look forward to have some results at the next report period.

FUTURE WORK

Future studies will focus on:

1.0. The effect of wood species on removal of metal ions
2.0. The effect of fungal hyphae of removal of metal ions
2.0. The kinetics of metal adsorption by wood.